Vol. XLV. March, 1911. No. 3

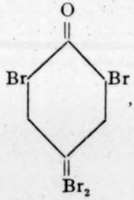
AMERICAN

CHEMICAL JOURNAL

ON THE CONVERSION OF BENZENESULPHONEDIBROMAMIDE INTO DIBROMBENZENESULPHONAMIDE BY MEANS OF CONCENTRATED SULPHURIC ACID.

By J. H. Kastle.

According to our present conceptions tribromphenol bromide and benzenesulphonedibromamide exhibit no analogies as to chemical constitution. Thus, according to Thiele and Eichwede[1] the former is a quinone derivative having the constitution



whereas benzenesulphonedibromamide,[2] as its name indicates, is a *N*-dibrom substitution product of benzenesulphonamide, having the formula $C_6H_5SO_2N.Br_2$.[1] As a matter of fact, however, these two compounds exhibit many analogies in physical and chemical conduct. Both are yellow in color, both melt within the same range of temperature, both are insoluble in water, but soluble in chloroform and other organic solvents. Both contain active bromine, both are unstable at temperatures slightly above their melting points. Both give up bromine slowly even at ordinary temperatures, under ordinary atmospheric conditions. Both readily liberate iodine from potassium iodide.

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[1] Ber. d. chem. Ges., **33**, 673 (1900).

[2] Benzenesulphonedibromamide was discovered by Hoogewerff and Van Dorp (Rec. trav. chim., **6**, 373 (1877)). It was afterwards prepared and studied by Kastle, Keiser and Bradley (This Journal, **18**, 4 (1896)) and still more recently by Chattaway (J. Chem. Soc., **87**, 145–171 (1905)). From a mixture of alcohol and water it crystallizes in lustrous, orange-yellow plates, melting at 110° and from chloroform in crystals melting at 116°.

The most interesting change of which tribromphenol bromide is capable, however, is that under the influence of concentrated sulphuric acid it undergoes a molecular rearrangement whereby it is transformed quantitatively into tetrabromphenol.[2] According to Lobry de Bruyn,[3] sulphur trioxide, and not sulphuric acid *per se*, is the agent primarily responsible for this transformation.

In view, therefore, of the many analogies displayed by tribromphenol bromide and benzenesulphonedibromamide, it seemed not unlikely that like the former the latter would also undergo a molecular rearrangement on treatment with concentrated sulphuric acid.

As a matter of fact, it has long since been pointed out by Chattaway and Orton[4] that substitution by the halogens in the benzene nucleus of aromatic amines and amides of the aromatic carboxylic acids is not a direct process, but one which takes place in two stages, in the first of which the hydrogen attached to the nitrogen is replaced by the halogen, the substituted halides thus produced then undergoing molecular rearrangement, with transfer of halogen to the benzene nucleus. Later Chattaway[5] and his coworkers succeeded in isolating many of these substituted nitrogen halides. They also succeeded in showing that many of these compounds could be preserved indefinitely under proper conditions, but that under the influence of catalysts, such as hydrochloric acid in glacial acetic acid, they are readily transformed into ortho and para benzene substitution products.

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[1] THIS JOURNAL, **18**, 4 (1896). See also Chattaway: J. Chem. Soc., **87**, 163 (1905).

[2] See Benedikt: Ann. Chem. (Liebig), **199**, 127; and also Kastle: THIS JOURNAL, **27**, 43–52 (1902).

[3] The reference to Lobry de Bruyn's work on this subject is inaccessible to me at the present time.

[4] J. Chem. Soc., **75**, 1046 (1899); **77**, 134, 789, 797, and 800 (1909), etc.; see also Chattaway: *Ibid.*, **86**, 1181 (1904).

[5] J. Chem. Soc., **86**, 1181, 1187 (1904).

Cohen[1] and his coworkers also have studied the action of sodium hypochlorite on the sulphonanilides and have arrived at the conclusion that the ultimate formation of *o*- and *p*-chlor substitution products is preceded by the production of *N*-chlor derivatives of the sulphonanilides. So far as I have been able to discover, however, no one has ever accomplished the molecular rearrangement of benzenesulphonedibromamide. In fact, according to Chattaway,[2] the *N*-halogen derivatives of the sulphonamides seem to possess greater stability than the corresponding derivatives of the aromatic carboxylic amides. It, therefore, seemed all the more desirable to see whether molecular rearrangement of benzenesulphonedibromamide could be accomplished by means of concentrated sulphuric acid.

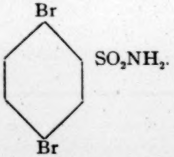
As a matter of fact it has been found that, at ordinary temperature, benzenesulphonedibromamide reacts instantly and somewhat vigorously with concentrated sulphuric acid. Only traces of bromine were liberated and the product of the reaction gave only traces of silver bromide on the addition of silver nitrate.

In my first experiment one gram of finely powdered benzenesulphonedibromamide was added in small amounts at a time, and with immediate mixing, to about 10 cc. of concentrated sulphuric acid. When larger amounts are added to the sulphuric acid the reaction takes place almost explosively and with the evolution of small amounts of bromine. The product of the reaction was poured into water. A white crystalline precipitate separated at once. This was removed by filtration and purified by crystallization from boiling water to which a small amount of animal charcoal had been

[1] J. Chem. Soc., **85**, 371–378 (1904).

[2] *Ibid.*, **87**, 145–171 (1905).

added. In this way there was obtained 0.5 gram of a white crystalline substance having the general properties of a sulphonamide. It was further purified by recrystallization from hot 95 per cent. alcohol. From this solvent it was obtained in the form of small, compact, glittering crystals, which under the low power of the microscope were observed to consist of well-defined, colorless, transparent, prismatic crystals. These were found to melt at 194°. For 0.2005 gram, heated with pure calcium oxide, were required 12.7 cc. 0.1 N silver nitrate, equivalent to 0.1015 gram bromine, or 50.62 per cent.; calculated for $C_6H_3Br_2SO_2NH_2$, 50.75 per cent.

On heating with lime considerable amounts of ammonia were evolved. There is no doubt, therefore, that this compound is a dibrombenzenesulphonamide, $C_6H_3Br_2SO_2NH_2$. Furthermore, it is more than likely that it is the *p*-dibrombenzenesulphonamide, 

This compound melts at 193°. On the other hand, the 1,3,4-dibrombenzenesulphonamide melts at 190°, so that further work will be required to settle definitely the constitution of the dibromsulphonamide resulting from the molecular rearrangement of benzenesulphonedibromamide. A second experiment was carried out in the following manner: Ten cc. of pure concentrated sulphuric acid were cooled to 0° and poured into a large porcelain dish which was placed on cracked ice. To this cold sulphuric acid there was added, in small amounts at a time, 4 grams of benzenesulphonedibromamide. As fast as the dibromamide was added it was intimately rubbed into the sulphuric acid with a porcelain pestle. In this way a mixture was obtained having the color and much the consistency of the yolk of an egg. After all of the dibromamide had been mixed with the sulphuric acid the dish was removed from the ice to the laboratory table and it and its contents allowed gradually to come to ordinary temperature. As a result of this slight rise of temperature the yellow dibromamide gradually dissolved in the concentrated sulphuric acid, giving rise to a clear light brown solution. In a short time, however, white crystals began to separate from the clear brownish solution, so that after 15 to 30 minutes the contents of the dish consisted of a white pasty mass of crystals. This pasty material was then poured into about ten times its volume of water and the white crystalline material thus obtained was collected on the filter and purified by recrystallization from hot water. This experiment was designed primarily to determine more accurately the quantity of dibrombenzenesulphonamide produced from a given amount of the sulphonedibromamide. Unfortunately the greater amount of this was lost during its purification by the breaking of a beaker. As nearly as I could judge from the bulk of the material, however, the dibrombenzenesulphonamide had been formed in large amounts and it is certainly the principal product of the change here under investigation.

As I have already pointed out, the filtrate from the dibrombenzenesulphonamide resulting from this rearrangement of the benzenesulphonedibromamide gives only a slight opalescence with silver nitrate, indicating the absence of hydrobromic acid or bromides. On evaporating this filtrate on the water bath, however, a small amount of a white crystalline substance was obtained. This substance is more easily soluble in water than the dibrombenzenesulphonamide above described. It melts at 135°–140° and also shows signs of fusion during its recrystallization from hot water. This compound has been found to contain only 36 per cent. of bromine. It also gives off ammonia on heating with lime. Up to the present, however, it has not been obtained in sufficient quantity to permit of its identification. Regardless of the nature of this second product, however, it is evident from these results that benzenesulphonedibromamide is largely converted into a dibrombenzenesulphonamide through the action of sulphuric acid. Such a change is of interest from several standpoints. I, therefore, hope to continue this investigation.

UNIVERSITY OF VIRGINIA,
January, 1911.

ON THE REACTION OF IODACETONITRILE WITH SILVER NITRATE.

By S. K. Loy and S. F. Acree.

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

Recent work[1] in this laboratory on the mechanism of the reactions of alkyl halides with urazoles, thiourazoles, and salts of these substances, and with sodium ethylate and sodium phenolate, has shown that in some cases the *anions* of the urazoles are the *chief* substances reacting with the alkyl halides. It appeared probable that the anion first unites with the alkyl halide and forms a complex anion[2] which then decomposes as follows:

$$\text{I. } CH_3I + \overset{+}{Ag} + \overset{-}{NO_3} \rightleftarrows \underset{\text{trace}}{CH_3I.\overset{-}{NO_3}} + \overset{+}{Ag} \longrightarrow CH_3NO_3 + \overset{+}{Ag} + \overset{-}{I}.$$

$$\text{II. } CH_3I + \left\{\begin{matrix} AgNO_3 \\ \text{or} \\ \overset{+}{Ag} + \overset{-}{NO_3} \end{matrix}\right\} \rightleftarrows \underset{\text{trace}}{CH_3I.AgNO_3} \longrightarrow CH_3NO_3 + AgI.$$

But in the case of certain thiourazole salts, of sodium ethylate and of sodium phenolate, Dr. F. M. Rogers, Dr. H. C. Robertson, and Mr. E. K. Marshall have found in work not yet described that the total reaction velocity can be expressed in terms of the concentrations of both the anions (reaction I) and the undissociated salts (reaction II). It had already been shown by Shadinger and Acree[3] that the alkyl halide probably reacts as a molecule with the urazole salts and apparently not as alkyl and iodide ions, as assumed by Bruyn and Steger,[1] nor as alkylidine and hydroiodic acid, as was supposed by Nef,[2] nor yet through the formation of a complex cation as was postulated by Euler.[3] The reaction of these nonionized[4] forms of the salts and alkyl halides had been foreshadowed, theoretically and experimentally, by Johnson and Acree,[5] who found that the transformation of acetylchloraminobenzene in the presence of hydrochloric acid takes place apparently almost entirely through the preliminary formation of an undissociated salt as follows:

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[1] Ber. d. chem. Ges., **41**, 3199 and earlier papers. This Journal, **43**, 505; **44**, 219.

[2] We are glad to mention that our colleague, Professor Heinrich Goldschmidt, has recently come to similar conclusions as a result of his researches on the alkylation of oximes, and has pointed out our prior views and experimental results (Z. Elek. Chem., **14**, 581; **15**, 10. Shepherd: Dissertation, Christiania, 1909). Professor Arthur Lapworth has held similar views for a number of years and has made them the basis of numerous important investigations (J. Chem. Soc., **81**, 1512; **85**, 48; **93**, 30).

[3] This Journal, **39**, 236–248.

$$CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \longrightarrow CH_3CONHCl_2C_6H_5 \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H} + \overset{-}{Cl}.$$

Shadinger and Acree[6] showed that in certain urazole reactions there could be at most only traces of the complex salt indicated in reactions I and II. It seems highly desirable to learn whether in any case evidence can be secured which proves beyond question that an appreciable amount of such a salt exists and we have taken up this study again. We have chosen this time the double compound obtained by Scholl and Steinkopf[7] by the action of iodacetonitrile on silver nitrate:

$$ICH_2CN + AgNO_3 \longleftrightarrow AgNO_3.ICH_2CN \longrightarrow AgI + NO_3CH_2CN.$$

This double compound exhibits in a qualitative way all of the properties demanded by the theory of reactions I and II, in that it can be easily converted back into the silver nitrate and iodacetonitrile, while, on the other hand, it can also be changed, even in the solid state, into silver iodide and cyanmethyl nitrate. The unsaturated nitrile group may aid in making the substance more stable. Professor Scholl kindly left to us the quantitative study of this question.

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[1] Rec. trav. chim., **18**, 325.

[2] Ann. Chem. (Liebig), **298**, 202–374; **309**, 126; **310**, 316–335; **318**, 1–57, 137–230; **335**, 191.

[3] Ber. d. chem. Ges., **39**, 2734.

[4] For the sake of simplicity we shall use the expressions "reactions of the ions or of the nonionized salts" instead of the more complex expressions involving the idea of a reaction velocity proportional to a constant and to the concentration of the ions or of the nonionized salt. There may be many steps involved in the change of the anion, or of this nonionized salt, into the end products, some of which will be discussed in our full reports.

[5] This Journal, **38**, 265; **41**, 461, and especially footnote 3, p. 462.

[6] *Ibid.*, **39**, 275–276.

[7] Ber. d. chem. Ges., **39**, 4393.

We have again chosen, as did Shadinger, the conductivity method in studying this problem, the assumption being that the complex salt is not more highly ionized than the silver nitrate, and that the complex ion, $\overline{NO_3 . ICH_2CN}$, must necessarily migrate more slowly than the simple nitrate ion. If these two reasonable assumptions hold, and if the complex salt is actually formed and decomposes slowly enough to be studied, we should have a lowering of the conductivity when we introduce iodacetonitrile into standard solutions of silver nitrate, the extent of the lowering depending upon the amount of complex salt formed. Of course, other methods should be used also to study this problem; namely, those involving the lowering of the freezing point, the rise in boiling point, the use of partition methods, the study of the ionic velocities, the use of electromotive force measurements,[1] etc., and we shall later use these. The data secured, however, if trustworthy, show that no appreciable amount of the double salt, $AgNO_3.ICH_2CN$, can be present when solutions of silver nitrate and iodacetonitrile in water, alcohol or acetone are mixed. This harmonizes with the kinetic data which others in this laboratory have obtained in all cases, and if this double salt, or its anion, yields the end products, the small amount present must decompose with a high velocity.

We shall continue to look for the presence of such double compounds in all of our studies, and shall investigate especially the following questions: (1) the concentration of the double salt; (2) the degree of ionization of the double salt; (3) the velocity of migration of the ions of the double salt; and (4) the velocity of decomposition of the double salt and its ions.

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[1] A similar study involving the hydrogen electrode is now in progress in this laboratory.

EXPERIMENTAL.

On the Reaction of Iodacetonitrile with Silver Nitrate.

The methods previously described for making the iodacetonitrile did not seem to give sufficiently good yields, and it appeared advisable to try to improve them. The plan followed was that of Scholl and Steinkopf,[1] Bauer,[2] and Henry.[3] Ethyl chloracetate, boiling at 143°–146°, was made from Kahlbaum's chloracetic acid and ethyl alcohol in the presence of sulphuric acid. The chloracetamide was obtained in 90 per cent. yield by treating the ester with 3 volumes of a concentrated solution of ammonia which was saturated with ammonia gas at 0°. The crude chloracetonitrile was obtained in nearly 100 per cent. yield by mixing the chloracetamide with a molecular equivalent of phosphorus pentoxide and slowly distilling off the nitrile. The iodacetonitrile was made by boiling the chloracetonitrile in three volumes of pure methyl alcohol with five molecular equivalents of potassium iodide (instead of two equivalents used by Henry) under a return condenser 12 hours (instead of 5 hours, as recommended by Steinkopf). The excess of alcohol was distilled off and the residue was poured into several volumes of water, whereupon a dark brown heavy oil separated out. This iodacetonitrile was washed with a solution of sodium thiosulphate to remove the free iodine and was then dried with anhydrous sodium sulphate. It can be purified by distillation under diminished pressure, the boiling point being 65°–67° at a pressure of 4–6 mm. The iodacetonitrile did not at any time distil over, nor remain, colorless, as the other authors state. The color, after four purifications and fractionations, was a light yellowish green, which, however, did not increase in intensity even after the oil stood eight months. By extraction with ether, some of the iodacetonitrile can be recovered from the wash water.

The complex salt, $AgNO_3.ICH_2CN$, was prepared according to the method described by Scholl and Steinkopf by allowing the iodacetonitrile to flow from a separatory funnel into a solution of silver nitrate in water. A light yellow precipitate settled out immediately, which, when separated from the solution, dried, and recrystallized twice from water at 50°, melted at 121°.

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[1] Ber. d. chem. Ges., **29**, 2417. Steinkopf: *Ibid.*, **41**, 2540. Braun: *Ibid.*, **41**, 2135.

[2] Ann. Chem. (Liebig), **229**, 167.

[3] Bull. soc. chim., **47**, 400.

The preliminary method chosen for studying the question whether appreciable quantities of the iodacetonitrile and silver nitrate form a double compound was, as stated above, the determination whether the conductivity of this mixture is different from that of a solution of silver nitrate having the same concentration. The concentration of the silver nitrate solutions varied from 0.1 N to 0.0025 N, and the values given are only approximately correct, as can be seen from the conductivity data. Since in each case, however, the same solution was used in the check experiments there is no doubt as to the validity of the conclusions. In each one of our preliminary experiments there was a precipitation of the complex salt or a formation of silver iodide. The conductivity was therefore lowered, as is shown in the following tables:

	μ.	Temp.
50 cc. 0.01 N $AgNO_3$ solution in water	63.52	0°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. water saturated with ICH_2CN	57.20	0°
50 cc. 0.005 N $AgNO_3$ solution in water	120.93	25°
25 cc. 0.01 N $AgNO_3$ solution and 25 cc. water saturated with ICH_2CN	95.67	25°

In methyl alcohol the same general results were obtained; in this case the precipitate formed was apparently colloidal in nature and clouded the whole solution:

	μ.	Temp.
50 cc. 0.02 N $AgNO_3$ in CH_3OH	70.42	25°
25 cc. 0.04 N $AgNO_3$ and 25 cc. 0.04 N ICH_2CN	48.59	25°

The results obtained in ethyl alcohol and acetone were exactly analogous to those cited above. Owing to the small solubility of silver nitrate in acetone 0.001 N solutions were used. Other similar results were obtained, but will not be given here.

Since in all of these solvents there was rapid precipitation of the double salt or of silver iodide, we made some very careful attempts to free the iodacetonitrile from all hydroiodic acid or other substance that would conduct the current in water, or that would react quickly with silver nitrate. This was done by shaking the oil several times with solutions of dilute alkali, and sodium thiosulphate, and then with small volumes of conductivity water until the aqueous solution showed no appreciable conductivity above that of the water. In this way approximately 0.1 N aqueous solutions of iodacetonitrile can be obtained which give no precipitate with silver nitrate at 0° or at 25° before 30 minutes. The conductivity of such a mixture can be easily measured, and when this is done it is seen that the conductivity of the mixture of silver nitrate and iodacetonitrile is not measurably different from that of silver nitrate in the same concentration.

The water used in all of the following experiments had a conductivity of not more than 1.83×10^{-6}, and corrections are, of course, made for this. The saturated aqueous solution of iodacetonitrile had practically the same conductivity as the water used. For instance, 50 cc. of one solution had a conductivity 2.0×10^{-6}, while another had the conductivity 1.96×10^{-6}. In the following experiments there was no precipitate nor cloudy appearance visible in one hour after mixing the solution at 0°, nor in 20 minutes at 25°:

	μ.	Temp.
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. conductivity water	70.1	0°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. water saturated with iodacetonitrile	69.98	0°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. conductivity water	125.1	25°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. water saturated with iodacetonitrile	125.1	25°

Similar experiments were performed in absolute methyl alcohol, which had a conductivity 2.3×10^{-7}. No visible precipitate was formed in 4 hours:

	μ.	Temp.
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. methyl alcohol	81.2	25°
25 cc. 0.02 N $AgNO_3$ solution and 25 cc. 0.02 N iodacetonitrile in CH_3OH	80.79	25°

Entirely analogous results were obtained by dissolving the pure double compound in these solvents and measuring the conductivities.

The results of these experiments lead us to the conclusion that no appreciable amount of the double compound,

$$AgNO_3.ICH_2CN,$$

exists in a solution of a mixture of silver nitrate and iodacetonitrile, or of the double compound, in water, acetone, methyl alcohol or ethyl alcohol. These conclusions may not be final, and, as stated above, we shall use still other methods in studying this question. The rapid precipitation of the double compound, $AgNO_3.ICH_2CN$, from aqueous and alcoholic solutions of the components must be due, therefore, to the small solubility of this substance and not to its appreciable concentration at any moment.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, June 1, 1910.

THE TITRIMETRIC ESTIMATION OF PHOSPHORUS IN SMALL AMOUNTS.

BY L. T. BOWSER.

A number of different procedures have been advocated and used for the determination of phosphorus in very small amounts, some of them good and others indifferent, but each apparently with some defect. With but one exception, so far as the writer has been able to gather from the literature of the subject, all these methods are colorimetric, the one exception being described by Veitch[1] in a short paper on the titration of small amounts. The objection to most of these colorimetric methods is the fact that any silica present in solution produces an effect similar to phosphorus, and on this account they are somewhat difficult of manipulation, and good results are by no means certain. A number of different investigations by the writer having shown the great accuracy and facility, under properly controlled conditions, of titration methods for the determination of small amounts of various other substances, it was thought that phosphorus should be capable of estimation by the same general procedure. With this in view, a short series of trials was carried out to see what would be the possibilities of such a method.

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[1] U. S. Bur. Chem., Bull. **90**, 188 (1904).

Veitch used for titrating the phosphomolybdate precipitate a standard hydroxide solution, one cc. of which was equal to 0.0005 gram P_2O_5. His results, while good as far as they went, were neither numerous enough nor obtained under sufficiently varied conditions to give definite conclusions for general work. His standard hydroxide solution was approximately N/6 in strength, and it seemed that by the use of a solution considerably more dilute very accurate results might easily be attained.

The first standard phosphorus solution used for these tests contained 1 milligram PO_4 per cc., or 1000 parts per million. Ten cc. of this solution was diluted up to one liter, so that 1 cc. contained 0.01 mg. PO_4, or 0.007474 mg. P_2O_5. Different volumes of this solution were taken so as to have present the desired amounts of phosphoric acid and in each case were evaporated to a volume of about 5 cc. before precipitating. To each was added about 0.2 gram of ammonium nitrate and 3 cc. molybdate solution. The standard alkali used was prepared from one regularly in use, and equivalent to 0.000179 gram P_2O_5 in 1 cc., by diluting 170 cc. up to 500 cc. Of this solution 1 cc. is equivalent to 0.00006086 gram P_2O_5. The phosphorus solutions were precipitated at 55°, kept at that temperature for one hour on the water bath, allowed to stand for two hours at room temperature, then filtered on a small asbestos pad about $^1/_{16}$ inch thick and washed with the usual wash solution containing potassium nitrate.

All titrations were carried out in exactly the same way as with larger amounts. The results of the first set are given in Table I:

Table I.

No.	Solution taken. cc.	P_2O_5 taken. mg.	KOH used in titration. cc.	P_2O_5 found. mg.	Dif. from original. mg.	Ave. dif. mg.	Ave. dif. Per cent.
1	10	0.07474	1.15	0.06999	—0.00475		
2	10	0.07474	1.35	0.08216	0.00742	0.00133	1.78
3	20	0.1495	2.30	0.1400	—0.00950		
4	20	0.1495	3.10	0.1887	0.3920	0.0148	9.90
5	30	0.2242	4.50	0.2739	0.0497		
6	30	0.2292	4.35	0.2587	0.0345	0.0421	1.78
7	40	0.2989	5.35	0.3256	0.0265		
8	40	0.2989	5.45	0.3317	0.0326	0.0295	9.87
9	50	0.3737	7.15	0.4473	0.0736	0.0736	19.70
10	50	0.3737	lost	....	....	....	...
11	100	0.7474	13.40	0.8155	0.0681		
12	100	0.7474	14.00	0.8521	0.1047	0.0864	11.56

After completing the titrations of this set a blank run was made on the asbestos used, although it had not been suspected that any error from this source was probable. However, four titrations required respectively 0.5, 0.45, 0.45, and 0.5 cc. potassium hydroxide, hence 0.5 cc. was subtracted from each titration result, giving the volumes noted in Table I, and bringing the results to a much more reasonable average than they at first appeared. Even with this correction, however, none of the results are good enough to show the capabilities of the method, on account of the decided irregularities that occur.

Another standard phosphate solution was now made up from C. P. microcosmic salt, with an approximate strength of about 0.1 mg. P_2O_5 per cc. of solution. When a determination of the actual strength was made, using for purposes of titration an accurately standardized caustic potash solution, 1 cc. of which was equivalent to 0.56 mg. P_2O_5, it was found necessary in every case to use 9.6 cc. of the alkali to dissolve the precipitate from 50 cc. of phosphate solution, thus showing a strength of 0.1075 mg. P_2O_5 for 1 cc. of the standard phosphate solution. Some trouble having been experienced, in a series not here recorded, with the settling down of molybdic acid in crystals, giving results entirely inaccurate, it was thought that perhaps too much molybdate solution had been used, hence a calculation, based on the amounts used in the "Official Methods," was made to learn the proper volume for use. It was found that 0.5 gram ammonium nitrate should be taken, and for 1 mg. P_2O_5 about 1.5 cc. molybdate, or 1 cc. for quantities less than 0.8 mg. For the second set, shown in Table II, the new phosphate solution was used, evaporated down as in the first set, and the phosphorus precipitated with the amounts of reagents just noted. Each was made up to a volume of approximately 10 cc. before precipitation in order to insure uniformity of conditions:

Table II.

No.	Solution taken. cc.	P_2O_5 taken. mg.	KOH used in titration. cc.	P_2O_5 found. mg.	Dif. from original. mg.	Ave. dif. mg.	Ave. dif. Per cent.
1	1	0.1075	2.45	0.1491	0.0416		
2	1	0.1075	2.65	0.1613	0.0538	0.0477	44.37
3	2	0.2150	3.85	0.2343	0.0193		
4	2	0.2150	3.95	0.2404	0.254	0.0233	10.37
5	3	0.3225	5.40	0.3286	0.0061		
6	3	0.3225	5.60	0.3408	0.0183	0.0122	3.78
7	4	0.4300	7.00	0.4260	—0.0040		
8	4	0.4300	7.10	0.4321	0.0021	—0.0010	—0.23
9	5	0.5375	10.15	0.6177	0.0802		
10	5	0.5375	9.45	0.5751	0.0376	0.0589	10.96
11	10	1.0750	18.05	1.0990	0.0240		
12	10	1.0750	17.85	1.0860	0.0110	0.0175	1.63

This set, too, exhibits considerable irregularity and cannot be considered as satisfactory, although several of the determinations are so. In order to ascertain as to whether the trouble could be attributed to the separation of molybdic acid, four blank tests were made, using 10 cc. of water and proceeding as usual. Decided amounts of the acid settled on the bottom of the beakers and wherever the stirring rods had been moved. Two of these required respectively 2.05 and 3.30 cc. of standard caustic potash (while from appearances the other two would have required even more), hence it seemed certain that here was where the trouble arose. Four more blank tests were then made, using in this instance 20 cc. of water and proceeding as usual. After deducting the correction for the asbestos it was found that no molybdic acid had settled in any of these, showing that the volume of solution when ready for precipitation should be not less than 20 cc. After thus locating the cause of difficulty another set was run which was in every way a duplicate of Set II, save that each solution was diluted up to about 20 cc. before precipitation. Following are the results, the correction for the asbestos having been 0.25 cc. in this case:

Table III.

No.	Solution taken. cc.	P_2O_5 taken. mg.	KOH used in titration. cc.	P_2O_5 found. mg.	Dif. from original. mg.	Ave. dif. mg.	Ave. dif. Per cent.
1	1	0.1075	1.90	0.1156	0.0081		
2	1	0.1075	2.20	0.1339	0.0264	0.0172	16.00
3	2	0.2150	3.95	0.2404	0.0254		
4	2	0.2150	4.10	0.2496	0.0346	0.0300	13.95
5	3	0.3225	5.80	0.3530	0.0305		
6	3	0.3225	5.50	0.3347	0.0122	0.0213	6.61
7	4	0.4300	7.30	0.4443	0.0143		
8	4	0.4300	7.05	0.4291	0.0009	0.0067	1.56
9	5	0.5375	8.75	0.5325	—0.0050		
10	5	0.5375	8.85	0.5386	0.0011	—0.0020	—0.37
11	10	1.0750	17.10	1.0410	—0.0340		
12	10	1.0750	17.15	1.0440	—0.0310	—0.0325	—3.02

These results were thought to be accurate enough for such work as is usually encountered; in fact it is doubtful if any better ones could be secured by any method, so attention was turned to its application in actual work. For this purpose a sample of floats was taken, containing silica, iron, aluminium and many other substances, in addition to phosphorus. One gram of floats was treated with nitric acid in the usual way to dissolve out the phosphorus, and the filtrate was made up to a liter, of which aliquot parts were taken up for the determinations. To 500 cc. of this solution was added 1.2014 grams of water glass, in order to make certain of having a fair amount of silica present, since tests on the original solution had failed to show the presence of any appreciable amount. Four aliquot parts of each solution were taken, each containing 25 cc., and the phosphoric acid determined by the usual volumetric method. One cc. of the potassium hydroxide solution used was equivalent to 0.00056 gram P_2O_5. Results were as follows:

Table IV.

No. 1 (without silica).		No. 2 (with silica).	
KOH. cc.	P_2O_5. Per cent.	KOH. cc.	P_2O_5. Per cent.
16.70	37.32	16.60	37.18
16.60	37.18	16.25	36.40
16.65	37.30	16.30	36.51
16.70	37.32	16.35	36.62
Average,	37.28	Average,	36.74

It will be seen that slightly higher results were obtained when silica was absent than when it was present. A 25 cc. portion of each solution was now diluted up to 250 cc. for estimation of the phosphoric acid by the proposed method. Four 20 cc. aliquot parts of each solution were taken, and the precipitation, washing, and titration carried out as in Set III, the results being as follows:

Table V.

Without silica.				With silica.			
No.	KOH. cc.	P_2O_5. mg.	Per cent. or parts per million.	No.	KOH. cc.	P_2O_5. mg.	Per cent. or parts per million.
1	11.95	0.7273	37.49	5	12.90	0.7851	39.25
2	12.30	0.7486	36.36	6	12.20	0.7425	37.12
3	11.95	0.7273	37.43	7	12.15	0.7395	36.97
4	12.15	0.7395	36.97	8	12.00	0.7303	36.52
		Average,	36.78			Average,	36.87[1]

These results are certainly quite satisfactory, and agree very closely with the values found by the regular volumetric method. Silica, it seems, does not appreciably influence the results, contrary to its behavior in the colorimetric methods and to the generally prevailing impression. The filtrates from the portions containing silica were of far greater color intensity than the others, having a deep yellow tint, but the precipitates were identical in appearance. It seems probable that the silicomolybdates formed at the same time as the phosphomolybdates are not precipitated, but remain in solution and are filtered off, hence if a proper excess of molybdate solution be present initially no trouble should be experienced by reason of the presence of silica.

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[1] Omitting No. 5.

It was now determined to take a still more dilute phosphorus solution and add more silica, to see if a large excess of the latter would really interfere. For this purpose an 83.33 cc. portion of each of the preceding solutions was diluted to 250 cc., thus making it just one-third as strong as before. To the one already containing silica was added 1.6367 grams more of water glass, making a total of 1.8369 grams in the 250 cc., as against 0.00833 gram of sample, and 20 cc. portions were used for precipitation. No flattering success marked this attempt, but the results may be instructive nevertheless. In the solution where silica was present the larger portion was immediately precipitated by the free nitric acid of the molybdate reagent, forming a gelatinous mass, which promptly clogged the filter and rendered subsequent filtration and washing excessively slow. Only two of these precipitates were filtered, requiring about two hours for each. Results were as follows:

Table VI.

No. 1 (without silica).		No. 2 (with silica).	
KOH. cc.	Parts per million.	KOH. cc.	Parts per million.
3.55	10.80	4.15	12.63
4.15	12.63	3.80	11.56
3.75	11.41		
4.25	12.93		
Average,	11.94		12.09
or	35.82 per cent.		36.27 per cent.

It is evident that the best conditions had been overstepped here, and that too small an amount of phosphoric acid was present, but, as before, it seems that silica did not affect the final results, hence no great caution in guarding against it is needed. From the standpoint of general utility it is believed this method will be found valuable, and it is hoped it may prove as useful to others as it has to the writer.

Briefly stated, the method is as follows: Use a convenient volume of solution, but see that when ready for precipitation it is not less than 20 cc. For less than 0.8 mg. P_2O_5 use 1 cc. molybdate solution, for more 1.5 cc. and 0.5 gram ammonium nitrate, precipitate at 55°, keep for one hour at that temperature, let stand for two hours, filter and wash. Titrate with a standard hydroxide solution not stronger than 0.02 N.

105 Grove St.,
Lynn, Mass.

THE RELATION OF OSMOTIC PRESSURE TO TEMPERATURE.[1]

By H. N. Morse, W. W. Holland and J. L. Carpenter.

PART II. THE MANOMETERS.

After the cells and the membranes had been perfected to such an extent that the solutions within could be relied upon to maintain their maximum pressures for weeks together, and to exhibit their original rotation when taken out, the problem of manometers assumed an altogether new importance; for they then became almost the sole measure of the possible further refinement of the work. With sufficiently accurate manometers at hand, there was no obvious reason why osmotic pressure should not be measured with a precision which would compare favorably with the best quantitative work in other fields. It was the conviction that, thenceforward, the principal problem was the improvement of these instruments which led the authors to devote over ten months to the preparation and verification of the manometers which were used in their latest attempt to determine the temperature coefficient of osmotic pressure. They are obliged to confess, however, that they are not wholly satisfied with the result. The reasons for this dissatisfaction will appear in connection with the various steps in the preparation of the instruments, likewise the remedies which it is proposed to employ in future work.

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[1] The work upon osmotic pressure which has been in progress in this laboratory during the past 10 years is aided by grants from the Carnegie Institution. The earlier papers will be found in This Journal, **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 257; **45**, 91.

To those who have had experience with manometers of very small bore, it is well known that the material which ordinarily passes for pure mercury in the laboratory is by no means suitable for manometric work, and that to obtain it in adequately pure condition for this purpose, one must take much more than the usual pains with its purification. The mercury used in our manometers—and also that which is now used in the bath thermostats—is cleansed in the following manner:

1. The commercial material is first filtered through paper filled with pinholes, to free it from dirt. It is then heated for four hours to the boiling point in a glass flask with a very long neck for the condensation of the vapors; and during this time a current of air is forced through the hot metal. On cooling, it is again filtered to remove the scum which usually forms in considerable quantity.

2. It is distilled in a vacuum.

3. The distillate is washed by the method of Lothar Meyer, but with water containing two per cent. of nitric acid and two per cent. of mercurous nitrate instead of a solution of ferric chloride. The apparatus in which the washing is done consists of a wide glass tube, two meters in length, to the lower end of which is fused a quite narrow tube of the usual double U form, the proportions of the descending and ascending limbs being so selected that the mercury which is used to support the cleansing liquid shall lie wholly within the smaller tube. To admit the mercury at the top and to regulate the flow, a separating funnel is employed, the lower end of which has been widened out into the form of an inverted funnel. Over this are tied two or three thicknesses of the finest silk bolting cloth. The material to be purified is thus made to enter the cleansing liquid in hundreds, and perhaps thousands, of excessively fine streams. It is passed *1000 times* through the solution of nitric acid and mercurous nitrate.

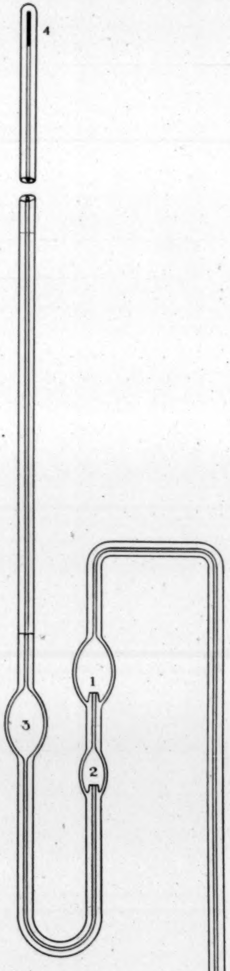

Fig. I.

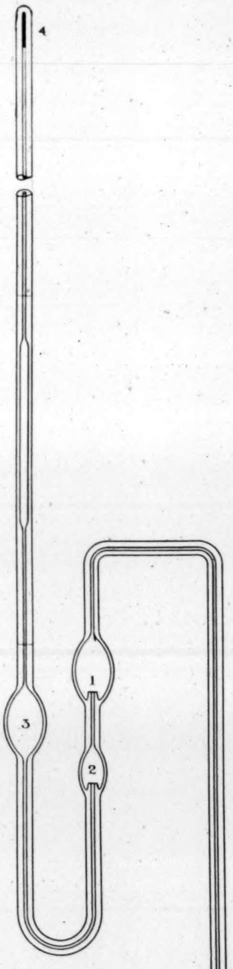

Fig. II.

4. After treating the mercury as described under (1), (2) and (3), it is washed with water, dried, and again distilled in a vacuum, but in a still which is used for no other purpose, *i. e.*, not in the still (2) which is used for the first distillation. The mercury which has been thus cleansed retains its brilliant luster in the air, and its movements in narrow tubes are highly satisfactory. We have also prepared the mercury for manometers from the purest oxide which we could make, but have not found the product superior in any way to mercury which has been purified as described above.

A paper[1] on the manometers then in use was published in 1908. But the practices of that time were modified so radically, in preparing for the recent work, that an entirely new presentation of the subject appears to be called for.

The form of the instruments which have been used in all the measurements to be presented in this series of papers is seen in Fig. I. The bore of these manometers varies from 0.45 mm., in the narrowest one, to 0.72 mm. in the widest one. The principal reasons for using tubes of very small internal diameters are:

1. In wide tubes, the short mercury columns (4, Figs. I and II) which fill the upper ends of the manometers are often dislodged by the severe tapping to which the instruments are subjected at certain times.

2. The compression of the small volume of gas which they contain involves but little dilution of the solution in the cell.

3. Relatively small volumes of mercury are required by manometers of small bore.

The disadvantages are:

1. It is more difficult to deal satisfactorily with the meniscus in a narrow tube.

2. The capillary depression is large in small tubes, and it varies so greatly with slight irregularities of bore that it is practically impossible to know exactly what correction is to be applied, except at those points in a tube where the capillary depression has been determined experimentally.

3. The movements of the mercury in small tubes are greatly

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[1] THIS JOURNAL, **40**, 325.

influenced by minute quantities of impurities, whether the same are dissolved in the metal itself or are attached to the surface of the glass.

Fig. II shows a form of manometer which has some distinct advantages over that seen in Fig. I. The volume of the nitrogen in such an instrument is relatively very large, a length of 1 mm. in the wider portion of the tube being about equal in capacity to a length of 16 mm. in the narrower part. The column of mercury which occupies the upper end is in the narrower part of the tube and is, therefore, not easily dislodged by tapping. In this respect, instrument No. II is not inferior to No. I. During a measurement of pressure by No. II, the whole of the nitrogen is compressed into the upper and narrower part of the manometer, hence the column of the gas is much longer for any given pressure than in No. I—so much longer, in fact, that unavoidable errors of meniscus and capillary depression become quite unimportant. In this respect No. II is greatly superior to No. I.

Manometers like that shown in Fig. II are designed more especially for the measurement of the pressure of concentrated solutions, where errors of meniscus tell heavily on the results unless large volumes of gas are used. In the case of dilute solutions, large gas volumes are obviously less necessary as a means of minimizing such errors.

The length of the wider portion of the second form of manometer is varied according to the pressure which it is desired to measure, *e. g.*, if the pressure in question is between 4 and 6 atmospheres, the wide and narrow parts are so related that the mercury meniscus will appear in the latter at some pressure slightly below 4 atmospheres. In instruments designed for use with normal solutions, on the other hand, the nitrogen is not all compressed into the narrower portion of the tube until a pressure of more than 20 atmospheres is reached.

No considerable increase in the dilution of the solution results from the larger volume of gas in such manometers, because, at the time of closing the cell, a mechanical pressure is brought to bear on the contents which is nearly equal to the osmotic pressure. Hence the subsequent diminution in the volume of the gas is small.

We have found the form of manometer represented in Fig. II much superior to that shown in Fig. I, but it is to be distinctly understood that the latter only has been used in the recent attempt to determine the temperature coefficient of osmotic pressure. Having once begun the work with the older style of instrument, it was thought that, whatever might be its faults, the errors resulting therefrom should affect all the measurements alike, rather than only a portion of them.

It will be noticed that two of the manometer bulbs are provided with "traps," 1 and 2, Figs. I and II. By means of these the mercury is made to enter the narrow tubes below at points somewhat above the bottom of the bulbs. The purpose of the arrangement will be understood from the following explanation: When the solution in the cell is under pressure, it enters to some extent the upper end of the nearest bulb (1), and when the pressure is afterwards removed and the mercury which had been previously expelled returns, it is apt to entangle minute drops of the solution between itself and the wall of the bulb. Occasionally one or more of these will persistently work its way forward towards the calibrated end of the manometer, making it necessary, sooner or later, to open, cleanse, and refill the instrument. The "traps" are an effectual preventive of such calamities. Before their introduction, it was necessary frequently to inspect the manometer for the presence of these migrating particles of liquid, and it happened, at times, that, notwithstanding the greatest vigilance, they escaped detection until it was discovered that the manometers were no longer measuring correctly.

The third bulb, 3, Figs. I and II, prevents the possible escape of nitrogen from the calibrated portion of the manometer. As stated already, the solution in the cell enters the upper end of bulb No. 1; and, before the instrument can be used for another measurement, it is necessary to remove the liquid which has thus made its way from the cell into the manometer, and, after washing the glass, to replace it either with mercury or with the solution whose pressure is to be measured. These operations involve a considerable diminution of the pressure on the nitrogen, and the purpose of the bulb (3) is to serve at such times as a safe reservoir for the expanded gas.

There are two very fine marks etched upon each manometer, one at or near the lower end of the calibrated portion of the instrument, and the other higher up. All data, whether they pertain to calibration or the measurement of pressure, are referred to one or the other of these marks. Two are made, because one of them is often out of sight in the bath, in which case the readings can be referred to the other. The exact distance between the two marks is known, hence readings which have been referred to one are readily translated into terms of the other. No graduation of manometers is attempted, because even the finest lines upon the glass interfere with the accurate location of the meniscus.

The short columns of mercury at the upper ends of the manometers, 4, Figs. I and II, serve to prevent contamination of the nitrogen while the instruments are being closed, and to keep the gas afterwards out of that portion of the tubes whose calibration has been affected to an unknown extent by fusing off the ends.

Fig. III represents an instrument which is in very frequent use in connection with the manometers. The manner of its use will be best illustrated by describing some of the operations in which it is most frequently employed:

1. Suppose the whole instrument, except the space occupied by the nitrogen, is filled with mercury, and it is necessary to cut off the tube between the bulbs 1 and 2, either for the purpose of replacing the detached piece by another of similar form, or by a simpler piece of glass tubing. The rubber-covered cone upon the open end of the manometer, or a sharply sloping stopper through which the end has been passed, is placed in the cup 1 (Fig. III). The air is then exhausted through a rubber tube attached to the stem at 2. When a sufficient quantity of mercury has been drawn into the cup, the whole arrangement is tipped backward until the

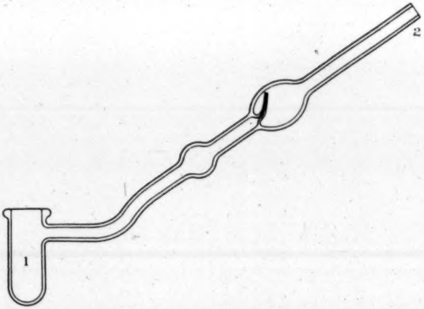

Fig. III.

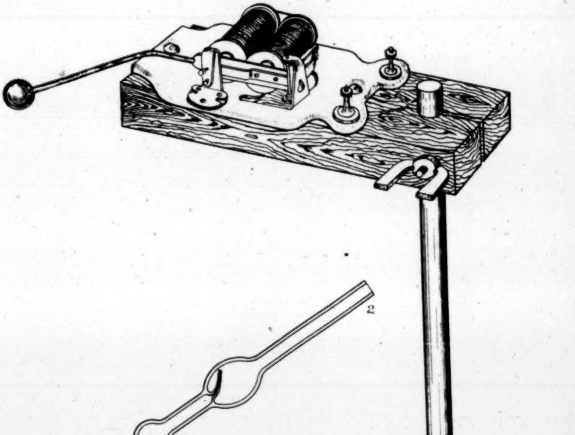

Fig. IV.

end of the manometer is exposed. Air is then cautiously readmitted to fill the space in the instrument which was previously occupied by the mercury.

2. Suppose the open end of the manometer, *e. g.*, to the middle of bulb No. 1, is filled with air and it is desired to replace it with mercury. A quantity of mercury is poured into the bottom of the cup, the manometer is inserted, and with the open end exposed, the air is exhausted, as before, through the rubber tube. On bringing the manometer again to the upright position so as to immerse the open end, and readmitting air, the mercury flows into the tube to replace the air which has been withdrawn.

3. Suppose, again, the manometer has been used in a measurement of pressure, and the open end—perhaps also a small portion of bulb No. 1—is filled with the solution. Before the instrument can be used in another experiment, this must be replaced, either by mercury or by some of the solution whose pressure is to be determined. The necessary manipulation will be readily understood from what has already been said. The course of procedure in the second case is as follows: (1) The solution is removed and replaced by air; (2) the air is replaced by the new solution, and this is, in turn, replaced by another portion of the same solution, etc., until there is no danger that the concentration of the new solution will be affected by the older one. If mercury is to be snbstituted for a solution, the tube must be washed and dried before introducing it. In this case portions of the wash liquids—water, alcohol and redistilled ether—are introduced and removed exactly in the same manner as when one solution is to be replaced by another. The final drying of the manometer is accomplished by attaching a tube containing a drying agent to the stem (2) and alternately exhausting and readmitting air.

Another important instrument is the "tapper" shown in Fig. IV. In a measurement, the mercury in the manometers has time enough to adjust itself to any pressure, but in operations connected with the calibration, comparison, and verification of these instruments, the "lag" of the mercury must be overcome by jarring the tubes, and frequently the tapping to which it is necessary to subject tubes of small bore is severe and prolonged. This is notably the case in manometers in which the glass is not perfectly clean, or has been slightly roughened by the reagents employed in cleansing it.

The construction of the "tapper" is so obvious that it is only necessary to notice two or three of its features. It is strongly inclined, when in operation, to move away from the tube which the "hammer" is striking. Hence the base is made of lead, for the sake of the greater weight, and is mounted upon three very sharp-pointed steel pegs which sink somewhat into the wood on which the instrument rests. The "hammer" is covered with rubber or leather to prevent the possible shattering effects of its blows. In the "*manometer house*," where all operations requiring a constant temperature and the use of the cathetometer are carried out, there are five of these instruments, each one of which is connected by means of a flexible wire cord with a hand push-button located at the cathetometer, so that the operator can tap any tube within the house without removing his eyes from the telescope.

The steel instrument seen in Fig. V is employed in determining capillary depression, in the calibration of manometers, in the determination of nitrogen volumes, and in the comparison of the manometers with one another or with a standard instrument. It is known—and for convenience will be referred to hereafter—as the "*steel block*." An instrument identical with it—except that it contained two places for manometers instead of three—has been described in a former paper.[1] The main feature of the block and the purpose of the various parts will be apparent on an inspection of the figure. It contains a reservoir (1) which is filled with mercury, and two plungers, one (2) large and the other (3) small. The larger one is employed for the coarser, and the smaller one for the finer, adjustments of pressure in the glass tubes 4, 5 and 6. The packing (7, 8, 9, 10 and 11), which

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[1] This Journal, **40**, 328.

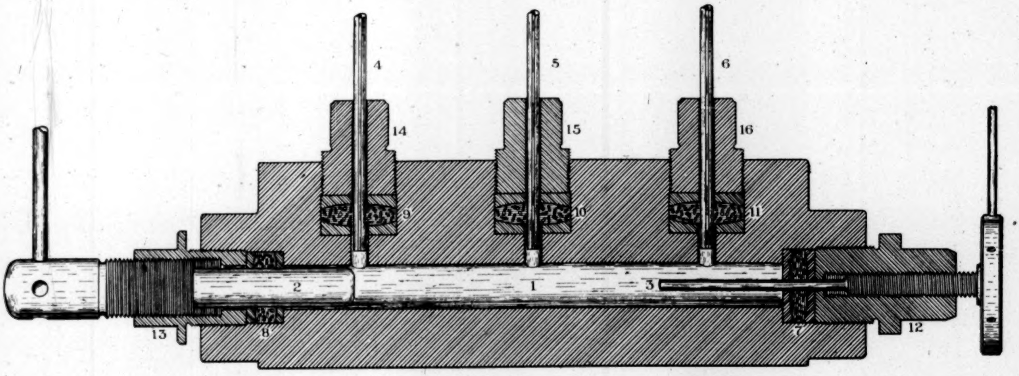

Fig. V.

may be of leather or rubber, or partly of both, is held, in each case, between the concave surfaces of two steel discs, and the required pressure is brought upon these by means of the threaded plugs 12, 13, 14, 15 and 16. The instrument has been tested and found to be *mercury-tight* up to 300 atmospheres.

Pure mercury only is put into the block, but it cannot be presumed, under the prevailing conditions, to maintain its purity; hence some precautions are necessary to prevent a possible contamination of the mercury in the manometers, or a fouling of the glass walls of the tubes near the open ends. The usual precaution, when a manometer is to be placed in the block, is to cut off the end (between the two bulbs, 1 and 2, Figs. I and II) and to replace the detached piece by another of suitable form and capacity, which is afterwards filled with pure mercury. When the manometer is taken from the block, the piece previously detached is restored to its place. A simpler way is to leave the manometer uncut and, after its removal from the block to draw out a large portion of the mercury and replace it with fresh mercury. This, however, involves the risk of fouling the tube and the necessity of cutting off the end afterwards for cleansing purposes.

The principal objection to the block is that, owing to the large mass of metal in it, its changes of temperature are very slow, and that, on this account, it is necessary to maintain a very constant temperature in the "manometer house" in which the block is located. It will be seen that with falling temperature in the block, however slight, a meniscus in a manometer which is under observation must always tend to take on a flattened or even a concave form, while, with rapidly changing temperature, whether upwards or downwards, a meniscus in the manometer cannot maintain a fixed position for any length of time. The obvious remedy is the maintenance of a perfectly constant temperature in the block, and this we attempt to accomplish by blowing over the instrument, day and night without cessation, a current of air of nearly constant temperature. The same difficulty is experienced, though in a lesser degree, with instruments of smaller mass.

Whenever occasion arises for a redetermination of the nitrogen volume of a manometer which has been used in the measurement of pressure, it is necessary, before placing it in the steel block, to remove the brass cone by means of which the manometer is fastened in the cell. Instead of melting the Wood's metal and separating the cone from the glass, it is customary to cut off a piece of the tube with the cone attached and to fuse on in its place for temporary use another piece of glass tubing. In this way a resetting of the cone is avoided. But, since the redetermination of the nitrogen volumes and the comparison of manometers in use are constantly recurring operations, much time and trouble are saved by using the "*brass block*" shown in Fig. VI. The internal arrangements of this instrument are precisely the same as in the steel block, except in the upper part where the manometers are inserted. There we have exactly reproduced in brass all the parts which are concerned in the closing of any cell after the manometer has been introduced. As a whole, the arrangement is, therefore, to be regarded as consisting of three brass cells, all communicating with a common reservoir, with facilities for bringing to bear on the liquid within any desired pressure. The manipulation involved in placing a manometer in the brass block is identical with that of closing a cell, and it is not necessary to remove the cone. The liquid used in the reservoir is either water or an aqueous solution of the substance whose osmotic pressure is being studied. One advantage of the brass over the steel block is that in it we have more nearly reproduced the conditions under which osmotic pressure is measured by the manometer, the principal difference being that the pressure exerted upon the nitrogen is mechanical instead of osmotic. It may be of passing interest to mention that the brass block, weighing about 25 kilograms, was made wholly from apparatus which was designed and found to be inadequate during the unsuccessful attempt to form the finished cell under pressure.

Fig. VII shows the arrangement of the "manometer house,"

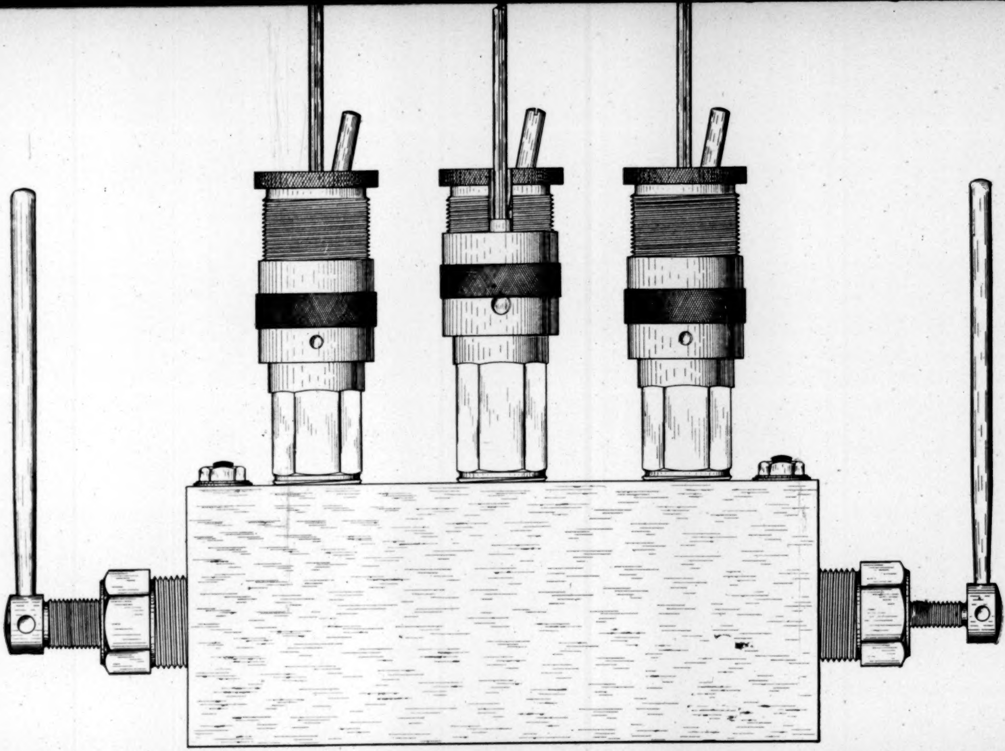

Fig. VI.

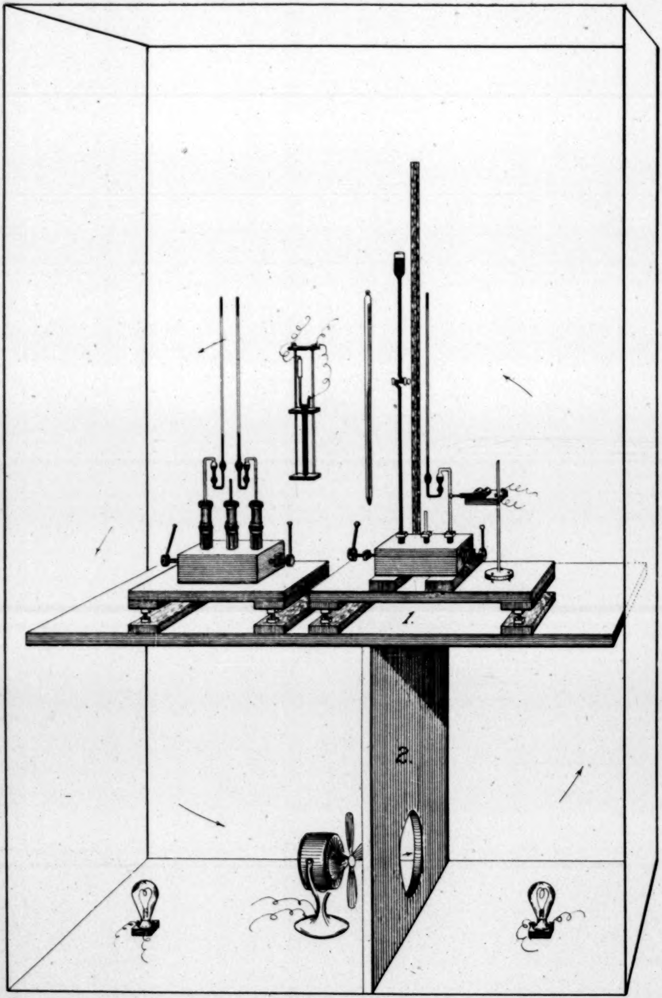

Fig. VII.

in which a constant temperature is maintained, and where all experiments on manometers, except calibration in the horizontal position, are carried out. It contains the "steel block," the "brass block," the "tappers," a meter scale, a thermostat for the regulation of temperature, electric heaters, and a fan motor, all of which will be recognized in the figure. The shelf 1, on which rest the various instruments, is supported by heavy brackets (not shown in the figure) which are bolted to the heavy masonry wall behind and afford a perfectly satisfactory degree of stability for the instruments. At each end of the shelf, a space 5 cm. wide is left for the passage of air. Lamps are employed as a source of heat for the reason that they heat up and cool down more quickly than other electric heating appliances. They are under the control of the thermostat seen in the upper part of the house. The fan is stationed before a hole of equal diameter in the partition 2. By means of it, the air, heated by the lamps, is kept in continuous circulation over all the instruments in the house. The temperature which is maintained in the compartment is always higher by a few degrees than the highest temperature in the room in which it is located.

The remaining features are better shown by the photograph, Fig. VIII, where the manometer house is represented with the plate glass front removed. The end to the right and the top of the house are also of glass, though the latter is usually covered with a thick woolen pad and the former with a flannel curtain. The front is also provided with a flannel curtain (not seen in the figure). The frame for the glass at the top is removable, to provide for the extension of the house upwards when very long tubes are to be accommodated. The various windows and doors are made to close tightly against rubber cushions, or the cracks between them and the framework are covered with surgeons' tape. The tubes through which the wires pass into the house are, however, left more or less open to provide for ventilation.

The type of cathetometer used in all our measurements is seen in Fig. VIII. Three such instruments are in use, one for each of the three large baths in which osmotic pressure is measured. The cathetometer here shown is also used in connection with a high temperature bath which is located on the right, but is not within view. Near the base of the cathetometer are the five hand push-buttons, by means of which the observer at the telescope controls the tappers within the house. Under the cathetometer is seen a specimen of the kind of foundation which supports all the baths and instruments concerned in the measurement of pressure. It consists of heavy wooden brackets. One end of the horizontal timbers is buried in the thick brick wall behind the house, while the descending timbers pass through the floor and enter the same wall in the room below. Two such brackets are required for a cathetometer and three for a bath.

The tubes which are used in making manometers are the most nearly perfect for the purpose which it is possible for us to obtain. The essential requirements are that any tube shall be of very nearly uniform diameter throughout, and that the form of the bore in every part shall be circular. Very few, if any, tubes conform perfectly to both conditions. Our tubes are imported in lots of several kilograms, and those who select them abroad are urged to spare no pains in procuring material of the highest possible excellence. In each lot of selected material thus obtained, we usually find—though not always—a few tubes which answer all reasonable requirements.

The first step in making a manometer is to etch upon the tube the two fine lines previously referred to as lines of reference ("upper scratch" and "lower scratch"). These are made no coarser than is absolutely necessary in order that they may be distinctly seen with the telescope, since a meniscus behind any line, however fine, is apt, in a small tube, to give the observer trouble. One of the lines is placed as near to one of the ends of the tube as an ample allowance of glass for subsequent operations will permit, and this becomes the "*upper scratch*." The distance from it of the second line, the "*lower scratch*," depends upon the length which the manometer is to have—ultimately, of course, upon the height of the available space in the baths. The calibration is begun at the lower scratch and is continued somewhat above the upper one. On

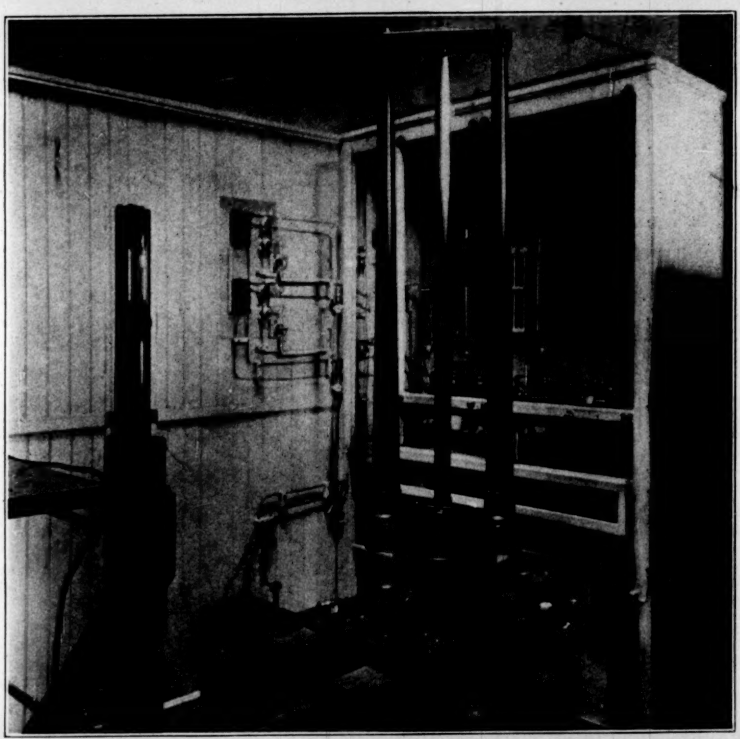

Fig. VIII.

the tube, below the lower scratch, and also on the end of the tube nearest it, is etched some common device for the purpose of identification. The tube is then cut between the two, leaving below the device, upon the part which is to be calibrated, enough glass for later operations. The detached end, having upon it the same device as the manometer, is carefully preserved. It was formerly used as a "*side tube*" whenever the volume of nitrogen in the manometer was to be determined or verified, also to settle at any time any doubts which might arise regarding the meniscus or capillary depression.

Near each end of the tube to be calibrated a small bulb is blown, which serves in case of accident to catch and save the threads of mercury which are used in calibrating the instrument in the horizontal position.

The next step is to determine the capillary depression at a number of places in the tube, all of which are located by reference to one of the scratches. In this operation the steel block is employed, and the side tube is either a very wide one or one whose capillary depression is already accurately known. The depression of the mercury in our narrowest manometer amounts to nearly 18 mm., *i. e.*, to more than 0.023 atmosphere. In those of medium bore, the depression amounts to very nearly 0.02 atmosphere In a carefully selected tube, the variation in capillary depression is not found to be sufficient to affect materially the measurement of pressure in concentrated solutions; but in the case of dilute solutions, it may amount to a sensible proportion of the magnitude measured. In the course of a calibration, we find the *mean* diameter of the whole tube, and we can, of course, at any time, calculate the *mean* diameter of short portions of it by means of the known weight and the observed and recorded lengths of the calibrating threads; but we are not able to deduce from the data thus far accumulated any safe rule by which the variations of capillary depressions in a tube can be derived from what is known or discoverable about the variations in the diameter of its bore. In other words, since it is not practicable to determine experimentally the capillary depression at every point in a tube, a part of the corrections which we apply for it may be to some extent erroneous. The error cannot, however, in any case, amount to a large proportion of the whole correction.

One method of calibration has been described in a former paper,[1] a brief outline of which will suffice for present purposes, since we shall probably abandon some of its features in future work. The manometer tube is placed in the steel block and nearly filled with mercury by advancing one of the plungers into the reservoir. A short thread of mercury is then introduced at the top, but so as to leave a cushion of air between it and the column of mercury below. The thread is lowered by manipulating one of the plungers until the bottom of the lower meniscus is opposite the lower scratch at which the calibration is to begin. In this position its length is determined. It is then raised until the bottom of the lower meniscus occupies the previous position of the top of the upper meniscus, when the length of the thread is again determined. The process of setting the thread end to end and of determining its length in each position is continued until the whole of the space which it is intended to calibrate has been covered. This done, the thread is run out of the tube and weighed. Afterwards, a thread of mercury filling the whole of the calibrated portion of the tube is introduced. Its length in the tube and also its weight are determined as in the case of the short thread. From the length and weight of the long thread. the mean diameter of the bore is calculated, and from the observations on the length of the short thread in the different parts of the tube, a calibration curve is constructed. Finally, a mean value for the meniscus is obtained from the length and weight relations of the short and long threads. It is clear that if we multiply the weight of the short thread by the number of times its length is contained in that of the longer thread, *i. e.*, by the number of times it was set end to end, the product will not be equal to the weight of the latter, and that the difference is the weight of the mercury which would be required to fill all the meniscus spaces which were left vacant in setting the short thread end to end up the tube.

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[1] THIS JOURNAL, **40**, 325.

Converting this difference in weight into volume, and dividing by the number of settings less one, we obtain a mean correction for a double meniscus, which is the meniscus correction to be applied in all our measurements of pressure, since the nitrogen in the manometers is always included between two mercury columns. This method of calibration is described in greater detail in the paper referred to above. It has been in less frequent use of late, principally because it requires the coöperation of two individuals and is less expeditious than the plan which has superseded it. The present mode of calibration differs from the older one only in the position of the tube during calibration and in the mode of shifting the threads. Instead of setting up the tube vertically in the steel block, it is placed in the horizontal position over a ruled mirror on the dividing engine. All the other features of the earlier method are retained, *i. e.*, the system of short and long threads, of setting the latter end to end, of finding a mean correction for the meniscus, etc. The manometers used in the present investigation were doubly calibrated, first in the vertical and then in the horizontal position. It is hardly necessary to mention the fact that the change in the mode of calibrating was preceded by a somewhat detailed comparison of the screw of the dividing engine with the graduation upon the meter scale.

Some innovations are necessary when a manometer of the form shown in Fig. II is calibrated. The narrower portions—below, from the lower scratch to the bottom of the wider part, and above, from the top of the wide part to the end of the tube—are calibrated with the same short threads, and the meniscus correction is obtained from the length and weight of a single long thread which fills the upper narrower portion of the tube. So far the method does not differ from that already described. It remains, however, to ascertain the capacity of the wider part as a whole, and eventually in terms of the calibration unit. To do this, the wider part is slightly more than filled with mercury so that both the upper and lower meniscus are well within calibrated portions of the narrow ends. From the weight of this mercury—with proper correction for overlapping in the narrower calibrated parts—

the total capacity of the wider part of the tube is calculated. Two verifications of the correctness of the previous work are now undertaken. It will be noticed, on referring to Fig. II, that the upper scratch is not very far above the upper end of the wider portion of the manometer. The first step in the verification is to fill the space between the two scratches with mercury—the upper meniscus may extend somewhat above the upper scratch. The volume of this mercury should, of course, be equal to the sum of the previously found capacities of all individual parts which were filled by it. The final step in the verification is to apply the same test to the whole tube by filling it with mercury from the lower scratch to the upper limit of the calibration.

The statement given above is believed to be ample enough to afford an accurate general view of the method of calibrating. The details of manipulation and the precautions which it is necessary to take at various points are omitted. There is, however, one matter which requires further consideration, and that is the *meniscus*.

The method of obtaining the meniscus correction which is given above is believed to be entirely correct in principle, but in applying it, *we have never found the meniscus to have the spherical form* generally ascribed to it. Usually the correction for meniscus obtained by the method described is just about three-fourths what it would be if the form were truly spherical. Sometimes it is slightly less and sometimes slightly more, but the values of what we will call the *experimental* meniscus always hover around this proportion of a spherical one. We are by no means prepared to dispute the assumption generally made that the form of the meniscus in narrow tubes is spherical, for the deviation from it which we seem always to find may possibly be due to errors in reading the length of the short threads which are used in calibration. If these are read always *too short*, the obvious result would be a too small correction for the meniscus. The following observation is of some interest in this connection and may throw some light on the matter. A beginner in calibration usually derives from his measurements a smaller meniscus correction than one who has had more experience; but as he continues his work under proper supervision, his corrections increase in value up to the limit mentioned, and thereafter his results will accord well with those of other experienced observers. Whether we do or do not "read too short" in calibrating, we are inclined to think that it is safer for us to use the "experimental correction" than that which is derived from the supposed spherical form of the meniscus; since, whatever unconscious errors we make in reading the length of the calibrating threads, we would be likely to repeat in measuring pressure.

The importance of the part which meniscus correction has played in the recent measurements of osmotic pressure may be judged approximately from the following statements: The *mean* final number of calibration units of compressed nitrogen in the manometers, for all the measurements upon the 0.1 weight-normal solution (at 0°, 5°, 10°, 15°, 20°, and 25°), was 124.72 (a calibration unit being the volume of the gas in a length of tube equal to about 1 mm.). The *mean* of all the corrections for a double meniscus was 0.176 calibration unit. That is, the mean correction for meniscus amounted to 0.141 per cent. of the total volume of nitrogen. The mean osmotic pressure of this solution, between 0° and 25°, was 2.5 atmospheres. The value of the mean correction for meniscus, expressed in osmotic pressure, was, therefore, 0.0035 atmosphere.

In the case of the weight-normal solution, the mean volume of the nitrogen was 16.916 calibration units, while the mean of all the corrections for meniscus was 0.1807 calibration unit. That is, the mean correction for meniscus was 1.07 per cent. of the volume of the nitrogen. The mean osmotic pressure of the weight-normal solution between 0° and 25° was found to be 25.95 atmospheres. The average correction for meniscus, expressed in osmotic pressure, was, therefore, *0.278 atmosphere.* For solutions of intermediate concentration, the value of the meniscus correction, expressed in osmotic pressure, varied, of course, between these limits, *i. e.*, between 0.0035 and 0.278 atmosphere. Stated in another way, the correction for meniscus in our work varied from 0.141 to 1.07

per cent. of the magnitude measured, according to the concentration of the solutions.

The question now arises, To what extent may these corrections have been erroneous? If we admit a possible error of 25 per cent. in the correction for meniscus, which seems to be ample, the proper statement would be: "The uncertainties due to meniscus correction range, according to the concentration, between 0.0009 atmosphere for the most dilute and 0.07 atmosphere for the most concentrated solution; or, if expressed in percentage of the magnitude measured, between 0.035 and 0.27 per cent." We are inclined, however, to regard the allowance of 25 per cent. for possible meniscus error as too large, since we cannot understand how an error of this magnitude could accumulate. It has been found that the independent readings of a manometer by two or more experienced observers will rarely differ more than 0.01 mm. Allowing this difference to be error, it would, in the case of the normal solution, amount only to 5.5 per cent. of the mean meniscus correction. There is still, however, to be dealt with that unexplained difference between the "experimental" and the supposedly spherical meniscus. The usual difference here *is* about 25 per cent. of the latter; but, as stated before, if we unconsciously read "short" in calibrating, we should again read "short" in measuring a pressure, and there are no more readings involved in deriving an "experimental" meniscus correction than in measuring a pressure; that is, the errors in question are not really of a cumulative character, as one might suspect at first sight.

One advantage of this mode of deriving a meniscus correction which should be mentioned is the excellent means which it affords of detecting faulty calibration. It is known that the best work in calibration leads uniformly to an approximately fixed value for the meniscus; hence it is to be inferred when another value is obtained, that the calibration which gave it is erroneous.

The degree of the accuracy of the meniscus correction has, however, but little weight in settling the particular question which we have been trying to answer, namely, *the relation of* *pressure to temperature.* Here an error of 50 per cent. in the meniscus correction, if uniform, would scarcely influence the solution of the problem, since the magnitudes compared in any case—the pressures of a given single concentration of solution at different temperatures—differ but little. To illustrate this point, we will consider the osmotic pressures of the weight-normal solution between 0° and 25°. The pressures which were found are tabulated below, together with the ratios of osmotic to calculated gas pressure at the various temperatures. The pressures given are the means of all the individual results at each of the six different temperatures, and the corrections for meniscus are likewise the *means* of all the corrections which were actually applied in calculating those pressures:

I. Temperature.	II. Osmotic pressures. Atms.	III. Cor. for meniscus. Atm.	IV. Ratio osmot. to gas pressure.
0°	24.825	0.238	1.115
5°	25.283	0.306	1.115
10°	25.693	0.293	1.113
15°	26.189	0.242	1.115
20°	26.648	0.307	1.115
25°	27.053	0.257	1.113

Suppose now that the extreme possible error has been made, and that the meniscus corrections given in the third column are *erroneous to the extent of 100 per cent.*, the pressures in the second column being *too small* by that amount. The following table gives the results corrected in accordance with that supposition:

I. Temperature.	II. Osmot. pres. + meniscus cor.	III. Ratio osmot. to gas pressure.
0°	25.063	1.126
5°	25.589	1.129
10°	25.986	1.126
15°	26.431	1.125
20°	26.955	1.128
25°	27.310	1.124

The ratios of osmotic to gas pressure given in the last column still agree to the third decimal place, and practically the same temperature coefficient for osmotic pressure would be derived from the values in both tables.

In view of the situation as explained above, we think ourselves justified in the conviction that our main conclusion—as to the *equality of the temperature coefficients* of osmotic and gas pressures within certain limits—is not sensibly vitiated by any possible errors in meniscus correction.

It is seen that, in determining the temperature coefficient, the errors in meniscus correction, if they are uniform, may be very large without seriously affecting the result; but when it is attempted to ascertain the relation of osmotic pressure to *concentration*, the case is very different, for then the pressures of all the various concentrations of solution are to be compared at fixed temperatures, and the meniscus corrections have consequently widely differing values. This is illustrated by the following tabulation of data taken from the record of a single manometer (No. 9). The meniscus correction (double) in this instrument is 0.17 calibration unit, and the volume of the nitrogen under standard conditions of temperature and pressure is 454.14 calibration units. Column I in the table gives the weight-normal concentration of the solutions; II, the pressures in atmospheres; III, the volume of the compressed nitrogen reduced to standard temperature; IV, the corrections in fractions of an atmosphere for the double meniscus; V, the relative osmotic pressures, the pressure of the 0.1 normal solution serving as the unit. Column VI contains the relative corrections for meniscus, the correction for the 0.1 normal solution serving as the unit. The temperature is in all cases 25°.

I. Conc.	II. Os. pres. Atms.	III. Vol. N_2. cc.	IV. Menis. cor. Atm.	V. Rel. os. pres.	VI. Rel. menis. cor.
0.1	2.635	141.15	0.00317	1.0000	1.0000
0.2	5.139	80.69	0.01083	1.9503	3.4164
0.3	7.738	55.59	0.02366	2.9366	7.4637
0.4	10.295	42.41	0.04126	3.9070	13.0158
0.5	12.947	34.01	0.06972	4.9135	21.9937
0.6	15.620	28.37	0.09360	5.9275	29.5268
0.7	18.436	24.11	0.12999	6.9928	41.0063
0.8	21.258	20.97	0.17233	8.1055	54.3628
0.9	24.126	18.53	0.22133	9.1558	69.8202
1.0	27.076	16.54	0.27834	10.2755	87.8044

Particular attention is called to columns V and VI, where it will be seen that, while the osmotic pressure increased a little over tenfold, the value of the meniscus correction increased nearly *88-fold.* At first sight, this enormous disproportion between the increase in osmotic pressure and that of the meniscus correction is somewhat startling to one who does not have clearly in mind the fact that, though this, in the first instance, is simply a space of fixed volume, its importance depends not only on the pressure upon the gas which fills it, but upon the *volume* of all the gas in the manometer as well.

Expressed in heights of mercury column, the correction for meniscus in the cases cited in the table increases from a value of 2.4 mm. to one of 211.5, and it is just these highly variable corrections which must be applied to the magnitudes to be compared in determining the relation of osmotic pressure to concentration. It is for this reason principally that we do not regard such relations as are shown in column V as being established with as much certainty as we think we have established the temperature coefficient within the field over which we have worked. And it was principally in order to determine the relation of pressure to concentration with a higher degree of precision that the form of manometer shown in Fig. II was devised. One of its purposes, as will be readily seen, is to minimize the importance of the meniscus, especially for concentrated solutions, without much sacrifice of the advantages of tubes of small bore. In the instrument prepared for use with weight-normal solutions, the final length of the nitrogen column is about 10 times as great as it is in the manometer which has been used in the investigation of the temperature coefficient. The gain in the direction of greater precision is obvious.

When the calibration of the tube has been finished, it is fused to the bent bulb tube (Figs. I and II) and filled with nitrogen. The purification of the nitrogen and the filling of the manometer have already been described;[1] and since very little change has been made in the procedure in either case, the briefest possible outline of these operations will suffice.

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[1] THIS JOURNAL, **40**, 325.

The gas is purified by passing air first through an alkaline solution of pyrogallol, and then, in the following order, over heated copper oxide, heated copper, heated copper oxide, fused calcium chloride, fused potassium hydroxide, and resublimed phosphorus pentoxide. The glass tubes containing the dry reagents are all connected with each other and with the receptacle for the nitrogen by fusing the ends together.

The apparatus used in filling the manometers is shown in Fig. IX. *A* is the reservoir for nitrogen. *B* is the manometer which is attached to the rest of the apparatus at *d* by fusing together the ends of the glass tubes. At the other end, the manometer is joined to the tube *C*, which serves as an air reservoir to keep the pure mercury in the instrument separated from that which is used in the rubber tube and funnel arrangement which is seen to the right. The side tube *f* contains the mercury which is to follow the nitrogen and remain in the top of the tube when it is closed. The somewhat complex process of washing and drying the manometer with purified air admitted through *h*, of replacing the air with nitrogen from the reservoir *A*, and of finally closing it with a short column of mercury in the top has been described in detail in the earlier paper on manometers. The only modification of the former practice which has been found necessary is due to the introduction of traps in two of the bulbs. When a tube with traps is first filled with mercury, minute quantities of air are sometimes left between the mercury and the glass in the bottom of these bulbs; and, if the angle between the trap and the side of the bulb is a sharp one, it is often difficult to dislodge the entangled gas. Hence it is necessary, before attaching the manometer to the nitrogen reservoir, to fill the bulbs and to remove any air which is imprisoned in the manner described. If the mercury afterwards runs out of the bulbs, no harm is done so long as the instrument is kept in the upright position, because the bulbs are then emptied only to the top of the traps. In the manometers recently prepared, the difficulty is overcome by giving a much flatter form to the bottoms of the bulbs with traps.

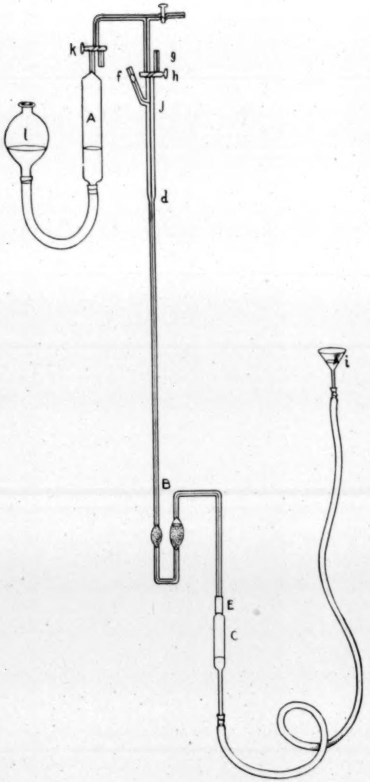

Fig. IX.

The volume of the nitrogen which has been introduced into the manometer is determined by means of the steel block. Formerly the instrument was placed in one of the three receptacles for tubes, and in another there was placed a piece which had been cut from the same tube, or, lacking this, another narrow tube in which the capillary depression had been determined at one or two points. If the piece of tubing which was to serve as a side tube was too short for the purpose, it was lengthened by fusing it to another similar tube. The third receptacle in the block was plugged with a glass rod or, preferably, occupied by another manometer—a so-called "standard" manometer.

The idea of using for the side tube a piece cut from the same tube as the manometer itself was, of course, that there would be no sensible correction for capillary depression. It was found, however, that the volume of the nitrogen—reduced to standard conditions—varied considerably with different positions of the meniscus, *i. e.*, with different pressures. In manometers of small capacity, these discrepancies have amounted, in extreme cases, to as much as one per cent. of the volume of the nitrogen. In the absence of any other known causes, it was necessary to ascribe such fluctuations in the apparent volume of the nitrogen to *variations in capillary depression* due to irregularities of bore. Moreover, it was apparent that in using a *narrow* side tube, we were in danger of multiplying, and possibly of more than doubling, the errors due to irregularities in the bore of the manometer itself. Hence, of late, when a nitrogen volume is to be determined, the narrow side tube is replaced by one having an internal diameter of about 30 mm., and much more attention is given to the investigation of the irregularities in the capillary depression of the manometers, that is, it is determined at many more points than formerly. The introduction of the wide side tube, in consequence of which only the errors of the manometer itself can now affect the results, has operated very favorably on the determination of nitrogen volumes, in that the volumes found under different pressures in any manometer are much more consistent than formerly.

We have used in our work until recently a so-called "standard" manometer. The third receptacle in the steel block was made for this instrument, and has most of the time been occupied by it. The "standard" differed from the other manometers, not in the pains which were taken with any one calibration, but in that the calibration was repeatedly verified. The use of the standard has not, however, given entirely satisfactory results. It has been impossible to make any other instrument conform to it absolutely. In other words, having found at some pressure the volume of the gas in a given instrument by means of the "standard," if we change the pressure, a slightly different value will be found, etc. The cause of the trouble is not difficult to discover. There is the same objection to the use of a "standard" manometer that there is to the use of a narrow "side tube," namely, that the results are vitiated by the errors of two instruments instead of one. It is for this reason that we now rarely use the "standard" manometer as a means of determining the volumes of gas in other instruments, or even for purposes of verification.

The difficulties which are encountered when a narrow side tube, or a standard manometer, is used reappear in full force when it is attempted to compare one manometer with another in the steel block, a practice very frequent in our earlier work, and still resorted to, but with less confidence than formerly. The osmotic pressures in duplicated determinations which are calculated from the original data of each instrument independently are rarely identical, as they should be. The discrepancies are not, however, large enough to weaken any general conclusions which may be based upon the measurements of osmotic pressure; but they suffice to explain, in large part at least, why it is that, with two perfect cells and two different manometers, we do not often appear to get quite the same pressures, though the concentration of the solution and the temperature are the same in both cases. It explains also why it is that duplicate measurements with one manometer generally agree better than those made with different instruments.

The necessity of making each manometer a law unto itself as regards accuracy, rather than subservient to some one standard for all, is unfortunate, for it greatly multiplies the pains and labor which must be bestowed on the individual instruments. The only alternative, however, appeared to be the employment of a "standard" with a bore wide enough to eliminate altogether the influence of capillary depression. The proper calibration and the use of such an instrument would obviously be attended with considerable difficulty, and we have not yet seen our way clear to undertake its preparation.

The following is a partial record of the capillary depressions which were found at different places in one manometer. The first column gives the distance above the lower scratch of the points at which the determinations were made, and the second, the depressions which were found at those points:

Distance above scratch.	Capillary depression.	Distance above scratch.	Capillary depression.
8.65	7.92	117.43	11.42
22.70	10.85	224.12	11.18
47.35	9.87	280.30	11.74
71.38	10.04	361.10	11.80
114.28	10.42	414.10	12.14

A difference of one mm. in capillary depression makes a difference of about one "calibration unit" in determining the volume of the nitrogen in a manometer. Suppose now the capillary depression of this tube had been determined only at the nine points beginning with the second one, 22.7 mm. above the scratch. The mean of these values is 11.05, which number would probably have been accepted as the *mean capillary depression* of the manometer. But suppose, when the volume of the nitrogen in the manometer is determined, the meniscus stands 8.65 mm. above the scratch, where the depression is 7.92 mm. The error, if the mean number 11.05 is used in correcting for capillary depression, is about 11.05 — 7.92 = 3.13 calibration units in the volume of the nitrogen. This example of what might happen if the condition of the tube at 8.65 mm. above the scratch had not been detected will serve to convince one, not only of the necessity of a most detailed investigation of the capillary depression in manometers of small bore, but also of the danger of using tubes of small bore or even "standard" manometers as "side tubes" when a nitrogen volume is to be determined. The whole volume of gas in the tube in question was 400 calibration units, hence the possible error in the case cited is 0.78 per cent., but to this there would have been added any errors of a *narrow* side tube, whether the same was originally a part of the same tube as the manometer itself, or a so-called "standard" manometer.

Capillary depression appears twice as an important factor in a measurement of osmotic pressure: (1) in determining the volume of the nitrogen under standard conditions of temperature and pressure, and (2), in correcting its volume under an unknown pressure which is the quotient of the two volumes.

The single illustration given above will suffice to give an idea of the possibilities in the way of error which pertain to tubes of small bore in consequence of their large and irregular capillary depression; and it will explain, in a measure also, why we felt obliged to confess at the beginning of this paper that, after ten months of labor bestowed on them, we were still dissatisfied with the manometers which were used in the attempt to determine the temperature coefficient of osmotic pressure. We were trying all of this time to use "standard" manometers and other tubes of small bore as "side tubes." The course to which we have finally been driven by the discrepancies which appeared is the one which we ought to have followed from the first, and would have followed if we had realized in the beginning the importance of the *variability* of capillary depression even in the most perfect tubes of small bore. The present procedure, so far as capillary depression is concerned, is as follows:

1. The tubes are calibrated with the utmost care with respect to capillary depression, that is, the capillary depression is determined at a great number of points in a tube, and a depression curve is made out which is quite as detailed as the curve for volume.

2. In determining the volume of nitrogen in manometers, the use of narrow side tubes and of other manometers has been abandoned, and only very wide tubes (30 mm. internal diameter) are employed for the purpose.

3. As in the case of meniscus, the relative effect of variable capillary depression is diminished by increasing the volume of the nitrogen. That is, the form of manometer shown in Fig. II has been adopted for the purpose of minimizing the importance of capillary depression, as well as that of meniscus.

4. Because the unknown errors of two instruments always add themselves in any direct comparison, the *verification* of one manometer by means of another (a "standard") has been given up, except as a means of detecting large errors, whatever may be their nature.

The question has arisen in our minds whether the slow contraction in glass, which is observed in thermometer bulbs, and which results in an upward displacement of the zero points, may not also affect our manometers, causing the volume of the nitrogen apparently to increase with time. We have been trying for two years to secure evidence on this point, but have been unable thus far to come to any definite conclusion. The trouble has been that the small differences which were apparently observed *might* be due to undiscovered irregularities in capillary depression. An effect of this kind is to be watched for, especially in the most recent form of manometer, where a wide tube is fused in between two narrower ones. These tubes are, however, annealed with care, and they are also allowed to lie for several months before a calibration is undertaken.

In conclusion, we will state that the whole time of one of the authors of this paper (C.) is given up to the study of the manometers which have been or are to be used in our measurements of osmotic pressure, and that we feel assured that no possibility of any very large error in this department of the work has escaped detection.

JOHNS HOPKINS UNIVERSITY,
December 24, 1910.

VISCOSITY AND FLUIDITY OF MATTER IN THE THREE STATES OF AGGREGATION AND THE MOLECULAR WEIGHT OF SOLIDS.

By Eugene C. Bingham.

[TENTH COMMUNICATION BEARING ON THIS SUBJECT.]

Introduction.

It is highly advantageous to consider the properties of matter under as varied conditions as possible. Many properties, however, are not as satisfactory in this respect as viscosity, which can be applied to all three states of matter. But, although it is now clear that gases and liquids and amorphous solids pass into each other without any sharp line of demarcation, when we come to consider the viscosity of matter in the three states of aggregation there are some very striking contrasts.

In liquids, the viscosity decreases with elevation of the temperature without a single exception; in gases, the opposite is the case without exception. In liquids, the viscosity seems to vary greatly with the density; in gases, the viscosity is independent of the density within wide limits. In liquids, the viscosity increases with the molecular weight; in gases, the molecular weight is of uncertain influence.

So with solids, the damping of the vibrations of a wire varies largely from substance to substance and with the temperature. This damping is of course far greater than can be accounted for by the friction of the air or by the loss of energy to the support. Hence this phenomenon, first studied by Weber, has been regarded by many, notably Lord Kelvin, as due to internal friction analogous to the internal friction or viscosity of liquids. Now it has never been made clear whether or not this *elastic after-effect*, as it is called, is in truth a measure of viscosity; and, as we shall see, there have even been some who have preferred to keep the two entirely distinct. In spite of this uncertainty, it seems clear that this loss of energy in vibrating is a true *frictional effect*. If, however, we regard it as a *measure* of the viscosity of solids, which appears to be the more usual practice, we find again a marked contrast with the viscosity of liquids with which it is supposed to be analogous.

In liquids, the viscosity decreases rapidly as the temperature is raised; in solids, the viscosity, as measured by the rate of damping of the vibrations of a wire, increases rapidly with the temperature. In liquids, the viscosity of a given liquid is constant for a given temperature and pressure. The fact that chrome alum solutions and some others suffer a change of viscosity on boiling, as well as a change of color and doubtless other properties, might be cited as exceptions to this, but the exceptions are not real because the different hydrates may properly be regarded as distinct compounds with their own properties. In solids, however, such exceptional behavior is the rule. It has been found that the viscosity as measured by the damping is greater when the wire is first loaded or if the wire is hardened, as in drawing. Rapid heating and cooling of the wire decreases the viscosity. Briefly, the viscosity of metals depends largely upon their history as well as upon their actual condition, which is thus quite in contrast with the behavior of liquids and gases, except for the readily explained exceptions noted above.

In our study of viscosity it now seems necessary, before proceeding further, to frame a hypothesis which will enable us to form some conception of the nature of the above phenomena and which will coördinate the apparently disconnected facts and suggest further study.

The Theory of Viscosity in Gases.

For gases, the kinetic molecular hypothesis is sufficient for the explanation of the principal facts, as is well known. If a gas is flowing over a plane surface, the gas which is actually in contact with the surface may, generally speaking, be considered to be at rest, since the smoothest surface must be considered quite rough in this connection. It has been proved that the velocity of the gas increases directly proportionally to the distance from the surface. Suppose *A* and *B* in Fig. I to be two layers of gas so thin that the translational velocity within each layer may be assumed to be constant. Let *A* be moving toward the right with a velocity very slightly greater than *B*. As the particles of the gas are moving in every direction, those of *A* will sometimes pass over into *B*, carrying with them not only their momentum due to their irregular motion, which is the same in both layers, but also the momentum due to the drift of *A* over *B*. Conversely, when particles of *B* pass over to *A* there will also be an expenditure of momentum required to impart to them the unidirectional motion of the drift. Thus, unless force is continually applied to *A*, it will come to have the same motion as *B*, *i. e.*, the unidirectional motion will all be changed into irregular molecular motion or heat.

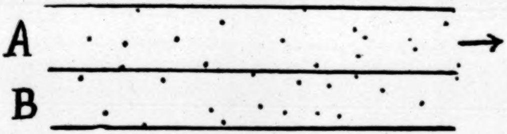

Fig. I.

As the temperature is raised, the irregular motion of the molecules becomes increased and the rate of loss of momentum is increased, *i. e.*, the viscosity is increased.

The fact that the viscosity of gases is independent of the density within wide limits was predicted by Maxwell as a deduction from the kinetic molecular hypothesis, which had been recently proposed. Its later verification by experiment constituted one of the chief arguments for the acceptance of the kinetic theory and is perhaps the most notable triumph yet achieved in the study of viscosity. The reason why the density of a gas does not affect the viscosity may be readily perceived. For as the density of the gas is decreased the same number of molecules cross the boundary between *A* and *B*, the only difference being that they come from a greater depth. This will not be true, however, when the molecules cross the confining space without encounter, and this breaking down of the law at very low pressures has been abundantly proved by experiment.[1] So also as the density is increased the mean paths become shorter and shorter but the number of molecules crossing the boundary between *A* and *B* remains the same, but this probably ceases to hold as the volume of the molecules becomes appreciable in respect to the spaces between them, or as the attraction between the molecules becomes appreciable, or, in other words, as Boyle's law ceases to hold.

The Theory of the Viscosity of Liquids.

For liquids, no consistent theory has been worked out, although oftentimes their viscosity has been referred to the attraction between the molecules. It does not appear, however, that such a theory can be worked out or that the attraction between the molecules in itself will suffice to explain the facts in regard to the viscosity of liquids. If in Fig. II we assume that *A* and *B* represent layers of liquid within which the velocity may be regarded as constant, while between *A* and *B* there is a very small velocity, then the conditions may be sufficiently well represented for our present purpose, which is rather to lay the basis for future work than to attempt a rigid mathematical presentation. The single molecules are to be considered as bodies of some appreciable size as compared with the spaces between them, although the question as to shape is left open. We must also assume that there is some attraction between the molecules, as proved by cohesion. Since the molecules are so much closer together than in the gas, the paths of the individual molecules must be

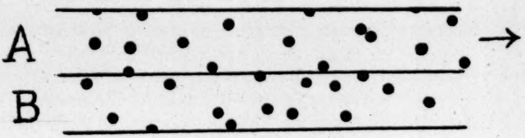

Fig. II.

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[1] Kundt and Warburg: Pogg. Ann., **155**, 337 and 525 (1875); **156**, 177 (1875).

exceedingly short, hence molecules with considerable translational velocity are unable to penetrate to layers with much lower translational velocity, so that the cause of viscosity in gases is not very potent in liquids.

Since the mean speed at any given temperature must remain the same, the number of molecules crossing the boundary between A and B will hardly be increased by any attraction between the molecules. Moreover, the forces of attraction are the same in every direction, so that no work is done within the liquid, and it is not apparent how the forces between the molecules can affect the viscosity.

Let us now digress for the moment to speak of external friction in order to obtain an analogy between external and internal friction that may be of service. If one body is resting upon another, forces of the nature of adhesion are exerted between the two, although for the most part the bodies will be separated by a layer of the atmosphere in which the bodies are immersed, but they will also come into contact at a few points. If force sufficient to cause the one body to move over the other is applied, the force required to keep the motion uniform is proportional to the force pressing the two bodies together, but it is independent of their size or their velocity, within certain limits, so long as the surfaces are the same; the smoother the surface, the less the friction. This much has been made clear as the result of a large amount of work. The friction is due to a variety of causes: (1) At the start adhesion has to be overcome to *separate* the particles which were in immediate contact, but after motion is established the force required to maintain the motion becomes less, and it is perhaps doubtful if the adhesion between the surfaces plays an important part. (2) Indirectly, however, cohesion plays an important part, for as the parts projecting from the opposite surfaces collide, particles are torn away, overcoming the forces of cohesion between them. (3) When a hammer strikes an anvil, a good part of its kinetic energy is transformed into waves of condensation and rarefaction which finally may be dissipated in heat. So as a solid moves over another, the projections of the one striking the projections of the other give rise to vibrations which may finally result in sound, light, electricity, or heat. Most of the friction apparently results from this last cause.

I believe that we may regard liquid viscosity or internal friction as the analogue of external friction, for if we think of the particles of *A* moving ever so slightly faster than those of *B*, then the particles of *B* near the boundary will be overtaken by those of *A*, and the latter will impart momentum to the former. The particle which has been thus overtaken, as in external friction, need not be carried along. It may first suffer a displacement, causing a condition of strain to be set up in its neighborhood. This strain later results in an increased molecular motion in *B*. It is this weakness of liquids in suffering displacement under stress that differentiates them from solids, but the line of demarcation is imperceptible. I shall speak later in this paper of the strain thus set up. According to this conception, the viscosity of liquids is not primarily dependent upon their cohesion, but upon the *volume* of the individual molecules, for the chances of collision between molecules of *A* and *B* will depend upon the ratio of the volumes of the molecules to the spaces between them. I use the term molecule, particle, or aggregate here without distinction. We might even include the term crystal with these when speaking of solids.

Connection between the Viscosity of Liquids and Molecular Volume.

It is evident that as the volume of the spaces between the molecules is still further decreased, the number of collisions will be increased. This is in harmony with the fact that in all liquids, without hardly an exception, the viscosity increases as the temperature is lowered, for the volume of liquids is thus generally decreased. Of course, if a change of molecular weight occurs, we may expect irregularity, hence we need not be unduly disturbed by such an abnormality as is shown in the density of water at 4°. In general, the relation holds good that as liquids expand the viscosity decreases. This is true, moreover, whether the expansion results from an elevation of temperature or a lowering of the pressure. Here again, however, water is abnormal at low temperatures, but the apparent exception can here be explained in the same way. It has been shown with certainty that viscosity increases with molecular weight, each atom having its own particular influence; and it appears that some groupings are of influence, the substance which has the more compact grouping having the least viscosity. Associated compounds have increased viscosity proportional to their association.[1] Colloidal substances, which have very large molecular weights, exert enormous influence upon the viscosity of their solutions. So also in mixtures, when liquids mix without marked volume change, the fluidities are a linear function of their composition[2], as we might expect. As far as I have been able to ascertain, whenever there is a marked contraction on mixing, as is true in very many aqueous solutions, there is invariably a marked decrease in the fluidity below what might be expected from the linear rule. In one instance I have observed that an increase of fluidity, in a similar manner, is connected with an increase in volume. It is regrettable that there are so few data with which to test this point. Yet various observers in other connections have noted a relation between viscosity and volume.[3]

In a recent paper[4] I pointed out that at some temperature near the critical temperature, the temperature coefficient of fluidity must be zero, *i. e.*, the fluidity must reach a maximum. The data of Warburg and Babo[5] enable us to say that for carbon dioxide such a maximum exists, within the limits of observational error, at the critical temperature and that for liquids, even in this limiting condition at the critical temperature, so long as the volume is constant the viscosity is independent of the temperature. While for gases the viscosity is independent of the volume within wide limits, for liquids the viscosity is apparently dependent primarily upon the volume. In gases the viscosity is dependent primarily upon the momentum of the molecules; in liquids, I have tried to show that it is dependent primarily upon the volume of the molecules.

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[1] Bingham and Miss Harrison: Z. physik. Chem., **66**, 1 (1909). Bingham: This Journal, **43**, 287 (1910).

[2] Bingham: This Journal, **35**, 195 (1906).

[3] Warburg and Sacho: Wied. Ann., **22**, 518 (1884). Bingham: This Journal, **43**, 287 (1910).

[4] This Journal, **43**, 295 (1910).

[5] Wied. Ann., **2**, 406 (1877).

The Theory of the Viscosity of Amorphous Solids.

For amorphous solids one would expect the same relations to hold as for liquids, since amorphous solids are nothing more than undercooled liquids. The difference should be one of degree only. As the temperature is lowered, the molecules continually get closer and closer, thereby circumscribing more and more each other's motion. The molecules, in suffering displacement, cause a state of strain to be established, as was pointed out above. As the cohesion of the substance increases, the stress which will be necessary to cause the displacement necessary for viscous flow also increases.

It should be noted here that if the displacement of a particle of *B* is sufficiently violent to cause it to be permanently displaced among its neighbors in that layer, the motion is no longer linear, and eddy currents are formed; and this motion does not obey the same laws as when the motion is linear, as has been abundantly verified. If, on the other hand, the stress accumulates faster than can be accommodated by the gradual breaking down of the strains here and there in the different layers of the substance, as has been explained, then the cohesive power of the substance will be exceeded and rupture will occur. In a rather viscous substance these accumulated strains may be observed, if the stress is removed quickly enough, by the springing back of the substance in the opposite direction to the stress. Moreover, this recoil will obey the laws of viscous flow in that its velocity will be directly proportional to the distance from the surface over which the fluid is moving and the velocity will be directly proportional to the strain. This recoil is the analogue of the "Weber effect" or "elastic after-effect" or "accommodation" in metals. Fortunately, this effect has also been observed for undercooled liquids as well. Barus[1] has measured the viscosity of marine glue by forcing it through a narrow tube after the method of Poiseuille. The glue was cut off at the opening of the tube, a series of cylinders being thus obtained. By weighing these, the rate of transpiration was determined. But the remarkable thing is that these cylinders did not keep their original cylindrical form, but a motion of the central axis of the cylinder, which continued for many hours, took place in the direction opposite to the stress, as shown in Fig. III. Trouton and Andrews[1] determined the viscosity of solid substances such as pitch and glass by continually twisting a rod or tube made of the material. They found that after the stress was removed there was a movement in the reverse direction for a long time. They then took the stress off as such a rate that there would be no movement at all. In this way the stress remaining at any given moment was a measure of the remaining after-strain. Plotting the time elapsed against the stresses, they obtained a rectangular hyperbola. Their experiment shows that the velocity of flow is proportional to the pressure, and the experiments of Barus indicate that the velocity is proportional to the distance from the surface over which the movement takes place.

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[1] Am. J. Sci., [3] **45**, 87 (1893).

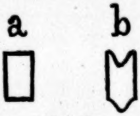

Fig. III.

As we may infer from the above and as I have pointed out elsewhere,[2] the fluidity of an undercooled liquid ought to approach the zero value asymptotically. So now we get a conception of the entire fluidity curve of a substance in relation to the temperature, as shown diagrammatically in Fig. IV. Starting with what must be practically zero fluidity at absolute zero of temperature the fluidity increases very slowly with the temperature from *A* to *B*, more rapidly from *B* to *C*, as a linear function of the temperature over a range *C* to *D*, then less and less rapidly, finally becoming constant at the

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[1] Phil. Mag., [6] **7**, 347 (1904).

[2] Z. physik. Chem., **66**, 238 (1909).

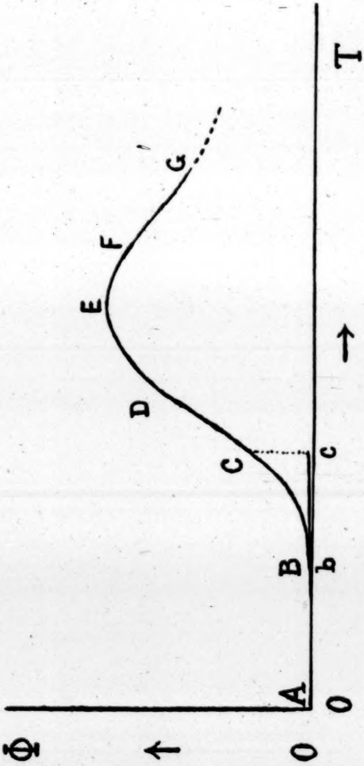

Fig. IV.

critical temperature *E*, and from that point decreasing over a range *F* to *G*, which has been explored. Beyond this we have no information, but it seems unthinkable, with our present knowledge, that a gas can become very rigid at even an exceedingly high temperature, hence we may assume that the curve does not cut the temperature axis at any point *H*. Substances are commonly regarded as solids over the range *AB*, as liquids over the range *BE*, and as gases from *E* on.

The Theory of the Viscosity of Solids.

We now will consider the solid state, meaning, by the term, the crystalline solid. We immediately see that in addition to the above curve, there must be for the crystalline solid another curve with very much lower fluidity over part of its course. This curve is entirely independent of the curve of the undercooled liquid, and corresponds to a substance with a very much greater molecular weight, this increase taking place at the time of solidification. This is shown in the curve *A b c*, Fig. IV.

Now turning to the case of wires subjected to torsional vibrations, we observe that the amplitudes of the vibrations form a geometrical series, hence the logarithmic decrement of the vibrations is the quantity which is usually sought. It has been found by Guye and Mintz,[1] as a result of their own experiments and of those of their predecessors, that if a wire is reheated with its maximum load, it will give a logarithmic decrement which is constant for a considerable amplitude at a given temperature, and the value is the same regardless of whether the immediately preceding values were at a lower or at a higher temperature. As was remarked at the beginning of this paper, there has been a tendency to consider this logarithmic decrement as a measure of the viscosity of solids analogously with the viscosity of liquids. This will be made clear from the following definition of the viscosity of solids taken from Thomson and Tait's *Treatise of Natural Philosophy*,[2] "A distinct frictional resistance against every change of shape is demonstrated by many experiments, and is found to depend on the speed with which the change of shape is made. A very remarkable and obvious proof of frictional resistance to change of shape in ordinary solids is afforded by the gradual, more or less rapid, subsidence of vibrations in elastic solids; marvelously rapid in India rubber and even in homogeneous jelly; less rapid in glass and metal springs, but still demonstrably much more rapid than can be accounted for by the resistance of the air. The molecular friction in elastic solids may be properly called *viscosity of solids*, because, as being an internal resistance to change of shape depending upon the rapidity of change, it must be classed with fluid molecular friction, which by general consent is called the *viscosity of fluids*." But even they recognized that the matter was not clear.

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[1] Arch. sci. phys. nat., [4] **26**, 136 and 263 (1908).

[2] Vol. I, pt. 2, p. 303.

Now it happens that steel and quartz show the smallest amount of damping, while a soft metal like lead shows a far greater amount. That lead can be considered to have a greater viscosity than hard steel, the term "viscosity" being used in its ordinary meaning, seems quite unbelievable. The difficulty is increased if we recall that the logarithmic decrement increases very rapidly with the temperature for most substances, and Guye and Freedericksz have shown[1] that at absolute zero of temperature the logarithmic decrement must become very nearly zero. This would correspond to infinite fluidity, which is certainly opposed to our usual conception of fluidity. Therefore it seems clear that although the damping of a vibrating wire is undoubtedly due to internal friction or viscosity, it cannot be used as a direct measure of that quantity.

If a filament of a perfectly elastic substance, to which quartz is the best approximation, were twisted away from its position of rest, it would come back to its original position even after the stress had been applied for a very long time; or if allowed to vibrate, it would swing back and forth for a very long time before coming to rest, the only losses of energy being to the support and the surrounding viscous medium. If an imperfectly elastic filament, like glass, be used, when it is twisted from its position of rest it will receive a "set," but if the stress is applied for a short time only, the set will be for the most part of a temporary character, and the glass will gradually creep back to nearly its old position of rest. This is the "elastic after-effect" of Weber. If glass then is allowed to vibrate transversely, the zero point *O*, in Fig. V, at the end of the first swing to the left is changed to *O′*, consequently, after the point, *O′* is passed, in returning the wire moves the remainder of the distance to *O* at the expense of its own momentum. Similarly at the end of the swing to the right the zero point has been changed to *O″*, and so on.

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[1] Compt. rend., **149**, 1066 (1909).

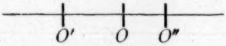

Fig. V.

It now becomes possible to form a conception of the phenomena taking place in a vibrating wire, and in elastic solids generally, on the basis of what we have learned from the viscosity of fluids. In twisting a wire, we can see from symmetry that the particles must move in circles, which are cross-sections of the wire, provided that the wire is round and homogeneous. Thus Fig. VI will represent a portion of a cross section, the layer *B* being the nearer the center. If the molecules of *A* move over *B* until the stress just balances the external force without the stress being relieved by even a partial breaking down of the material, then there will be no loss of energy by internal friction and when the external force is removed the material will return to its original position. In other words, if the molecules of *A* push against those of *B* but fail to pass them, as they do pass in the case of viscous flow, then the material is perfectly elastic. But it seems likely that all substances with which we are acquainted will

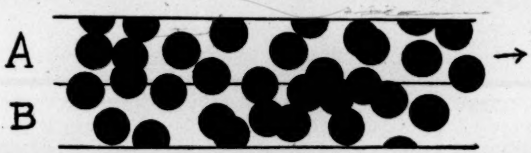

Fig. VI.

flow like liquids if sufficient pressure is applied for a long enough interval of time. The pressure which is necessary to make the flow perceptible is the "elastic limit," but the flow is so very slight that a wire loaded to the elastic limit may still bear a somewhat increased load without at once breaking, so that the "yield point" lies somewhat beyond the elastic limit. When this point is reached the wire is no longer able to sustain even its former load and rupture takes place as explained earlier. According to this conception the greater the damping the greater is the *fluidity* of the substance! This view is in harmony with the fact that the logarithmic decrement increases with the temperature, for the fluidity may be expected to increase as the molecular distances are increased. Further tests of the above hypothesis as applied to solids will be given further on.

Having already reached the above conclusion in regard to the error of regarding the logarithmic decrement as a measure of viscosity or internal friction in solids, I was delighted to find that Kuppfer, as early as in 1861, had held the view that the damping of a wire is a measure of its fluidity and stated it in such a convincing manner that Pearson at a much later date, 1893, recognized the difficulty of regarding the after-strain as a measure of viscosity, and advised against it in the following words: "It seems difficult to me to identify frictional resistance and elastic after-strain."[1] He goes on to say that "the creeping back to the original shape which goes on, it may be for minutes, hours, or even days, after the removal of the load, can hardly be due to frictional action," but, as we have seen, the work of Barus and of Trouton and Andrews throws a flood of light on this point. This difficulty in regard to elastic after-strain also troubled Kuppfer, for he says: "Die Nachwirkung bringt hier dieselbe Wirkung hervor, wie die Friction beim Widerstande der Luft, und besteht wohl auch in Nichts anderem, als in einem mit Friction verbundenen Glitschen der Theile über einander: nur ist nicht zu übersehen, dass die Friction der Theilchen unter einander nicht zu erklären im Stande ist, warum der Stab oder der Draht, nach Aufhebung der ablenkenden Kraft, wieder zu seinem ursprünglichen Gleichgewichtszustande zurückkehrt; diese Erscheinung setzt offenbar eine gewisse Kraft voraus, welche jeden festen Körper, selbst wenn er durch Änderung seiner Form in andere Gleichgewichtsbedingungen versetzt worden ist, dennoch immer wieder in längerer oder kürzerer Zeit zu seiner ursprünglichen Form (oder zu seinen ursprünglichen Gleichgewichtsbedingungen) zurückfährt, wenn die Abweichung von der ursprünglichen Gleichgewichtslage nicht gar zu gross gewesen ist."[1] This statement by Kuppfer causes Pearson to remark that "This passage seems to me to mark off the real distinction between after-strain and any frictional action between the parts of the body, and I think destroys the force of the comparison of a solid body's elastic after-strain with fluid action. It is a strong reason for not allowing elastic after-strain to be masked under the term viscosity." I believe that all of the difficulties are removed by means of a conception like the one that I have outlined. How clear Kuppfer's conceptions were for the time in which he wrote may be inferred from the following: "Il paraît que les molécules des corps solides possèdent la propriété non seulement de s'écarter les unes des autres en produisant une résistance proportionelle aux écarts, mais aussi de glisser les unes sur les autres, sans produire aucun effort. Cette propiété est possédée à un haut degré par les fluides; je le nommerais volontiers la fluidité des corps solides; le coefficient ψ pourrait être appelé coefficient de fluidité; la malléabilité des métaux paraît en dépendre et peut-être aussi leur dureté; des expériences ultérieures nous apprendront jusqu'où va cette analogie."[2]

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[1] Todhunter and Pearson: "The History of the Elasticity and Strength of Materials," Vol. II, pt. 2, Sec. 1718, p. 419.

We use the term fluidity in respect to solids as did Kuppfer and note with him that there are other terms in use which are evidently closely related, as malleability, pliability, and softness, while the reciprocals of these find expression in the terms viscosity, internal friction, rigidity, and hardness. Elasticity of shape seems to depend not only on a high viscosity, but also directly on the cohesion between the molecules. Barus seems to have regarded the two as merging into each other, believing that the more highly viscous a substance is the greater is its elasticity of shape. There appear to be, however, four categories into which substances fall, depending upon the possession to greater or less degree of the above two properties. (1) There are substances possessing high cohesion and high viscosity, as steel and quartz. (2) There are others possessing high cohesion but relatively low viscosity, as India rubber. (3) Substances with low cohesion and low viscosity are represented by most liquids and gases; while (4) there are substances of low cohesion and high viscosity, as is the case with many inorganic salts, like sodium chloride which has not been made to flow even under the highest attainable pressure.

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[1] Mém. Acad. St. Pétersburg sci. math. phys., [6] **6**, 397–494 (1857).

[2] Recherches expérimentales sur elasticité des métaux faites à l'observatoire physique central de Russie, p. 50 (1860).

Rubber is highly elastic yet the damping of its vibrations is marvellously rapid, showing a high degree of fluidity. The easy elongation of rubber is also an evidence of its fluidity. There is the utmost range in both of these properties so that all of the above examples are not equally good and it may be said that most substances fall between the extreme cases enumerated.

Finally it will be worth while to test the above hypothesis to see if it will explain the peculiar behavior of solids.

(1) Increase in temperature will cause the molecules to be separated, generally speaking, so that the fluidity will be increased, which has been found true for a considerable number of substances, as marine glue,[1] ice, glass,[2] and, as we have seen, the same is probably the case with most metals. Quartz is exceptional in this respect but its expansion coefficient is also exceptional, which may provide an explanation.

(2) Pressure has the effect of decreasing the fluidity, as we would expect. Barus has shown that for marine glue the effect of one degree rise in temperature requires the effect of

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[1] Barus: Phil. Mag., [5] **29**, 337 (1890).

[2] Trouton and Andrews: *Loc. cit.* Weinberg: Ann. Physik. [4] **18**, 81 (1905).

many atmospheres of pressure to counteract it. This is in accordance with the relative effects of temperature and pressure on volume.

(3) Repeated heating and cooling, according to Horton,[1] causes a decrease in the logarithmic decrement which may be interpreted as due to the increase in the elasticity of the metal, on account of the removal of the strains originally present.

(4) When a wire is first loaded strains are developed, hence vibrations take place by means of viscous flow to a larger extent than after the wire has hung for a long time when the strains have become more equally distributed. So the logarithmic decrement decreases with time.[2]

(5) For large amplitudes of swing the logarithmic decrement is greater than for small amplitudes,[3] because the nearer the limit of elasticity is approached the greater will be the amount of motion of the viscous kind.

(6) But if the vibrations are continued rapidly for a long time residual strains will accumulate to such an extent that elastic motion will be largely prevented, giving a state of "elastic fatigue" discovered by Lord Kelvin. Thus a steel tuning-fork vibrated continuously for many hours will reach a state where it will hardly vibrate at all, as has come under my own observation.

(7) Heating will dissipate the above "fatigue" because thereby the strains are removed. Resting will accomplish the same result, in the course of time, by means of the more leisurely viscous flow at the lower temperature.

(8) Trouton and Andrews[4] have shown that if a rod of such solids as glass, pitch, etc., be twisted with sufficient force, the parts of the rod may be made to move continuously over each other with a velocity which is greatest at first but gradually decreases to a constant value. This is explained by the after-strain requiring time to reach its maximum, just as we have seen that it dies away slowly in these substances.

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[1] Phil. Trans. (London), **204**, A, 1 (1904).

[2] Guye and Mintz: Arch. sci. phys. nat., [4] **26**, 136 and 263 (1908).

[3] Guye and Mintz: *Loc. cit.*

[4] Phil. Mag., [6] **7**, 347 (1904).

Other tests of a similar character will readily suggest themselves, such as the cause of the increase in strength of wires on drawing. It even becomes possible to form a conception of the perplexing behavior of plastic substances, like clay, which do not yield at all until a certain pressure is reached, when they yield rapidly. The resistance at first is probably due to the adhesion between the particles. This adhesion will be the more considerable, because the particles are very small and their surfaces correspondingly great. When, however, the particles become separated, the resistance is largely dependent upon the viscosity of the medium filling the spaces between the particles, as, for example, water, in the case of plastic clay. The fluidity of mixtures of substances which are insoluble in each other presents a very interesting field for study. Moreover it has important technical bearings, as in the manufacture of paints, lubricants etc. One phase of this subject is now being studied experimentally by Dr. George F. White and myself.

In conclusion, I venture to express the belief that the viscosities of solids may be measured in such a way as to obtain results which are comparable with those obtained for liquids and gases. For undercooled liquids the methods of the falling sphere and of forcing the liquid through a capillary tube have been tried with success.[1] The viscosity of the more highly viscous bodies may probably be measured by the methods tried by Trouton and Andrews, of continuously twisting a rod or tube, of determining the sagging of a beam, or finally of measuring the vibration of a wire.

If these methods can be made to give comparable results, as has been indicated by the work of Trouton for all except the last method, then it seems quite possible to solve the problem of obtaining the molecular weights of solids, which has baffled us thus far, since the method of getting the molecular weights of liquids by means of their viscosities[2] has been found to give good results.

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[1] The latter method has been applied to metals by Werigin, Lewkojeff, and Tammann: Ann. Physik, [4] **10,** 647 (1903).

[2] Bingham: Z. physik. Chem., **66,** 238 (1909).

THE DISSOCIATION OF ELECTROLYTES IN NONAQUEOUS SOLVENTS AS DETERMINED BY THE CONDUCTIVITY AND BOILING-POINT METHODS.

BY HENRY R. KREIDER AND HARRY C. JONES.

Four methods have been devised for measuring the dissociation of salts in solution: The conductivity and freezing-point methods, the solubility method of Nernst and Noyes, and the boiling-point method. Of these the conductivity and freezing-point methods are the best known, and are the most accurate. The solubility method of Nernst and Noyes is not widely applicable. Within recent years the boiling-point method has been so much improved by Jones and others that it gives fairly accurate results.

There are certain objections to all of these methods. The conductivity and the freezing-point methods give good results in aqueous solutions, but in nonaqueous solutions which are less dissociated, their use has been attended with difficulty. In many of these solvents it has not been possible, previous to the present time, to determine μ_∞ accurately, and, consequently, the dissociation could not be calculated from the results obtained by the conductivity method. Many of the nonaqueous solvents freeze at a temperature so far below the ordinary that the application of the freezing-point method is often impossible.

By means of the latest type of cell devised in this laboratory, and which will be described later, we have been able to measure μ_∞ for a number of salts in methyl and ethyl alcohols, and thus to calculate the dissociation of these salts in these solvents from the data obtained by the conductivity method. The dissociation of these same salts in the same solvents was determined by the boiling-point method with the object of finding if any relation exists between the results obtained by the two methods.

HISTORICAL REVIEW.

A large amount of work has been done with nonaqueous solvents, especially with the lower alcohols of the aliphatic series. These were soon found to have the property of dissociating salts to a considerable extent. Fitzpatrick[1] studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride and calcium chloride in both methyl and ethyl alcohols, and found values which were considerable, though less than those in water. Hartwig[2] measured the conductivity of a number of organic acids in both methyl and ethyl alcohols. Paschow[3] worked with potassium iodide, cadmium iodide, calcium iodide, potassium acetate and sodium acetate in methyl alcohol. Vicentini[4] measured the conductivities of a number of salts of these alcohols. Cattaneo,[5] working with salts in ethyl alcohol, found that a number of those with which he worked have a negative temperature coefficient in this solvent. Vollmer[6] studied several salts over a large range of dilutions. Holland[7] investigated the effects of nonelectrolytes on the conductivity of various salts in methyl alcohol. Carrara's[8] work is very important. He carried out an extensive investigation on a large number of salts in methyl alcohol. Walden[9] did a large amount of work with pure organic solvents. The work of Dutoit and Aston[10] and of Frederich[11] is important. They formulated the hypothesis that the dissociating power of a solvent is a direct function of its degree of association in the pure state. Other workers in this field are Kablukoff,[12] Vollmer,[13] and Kahlenberg and Lincoln.[14]

Mixed Solvents.

Wakeman[15] carried out an investigation on organic acids in mixtures of water and ethyl alcohol and found that the conductivity of these substances in these solutions decreased with increasing amounts of alcohol. Zelinski and Krapiwin[1] point out that the salts with which they worked, the iodides and bromides of sodium and ammonium in mixtures of 50 per cent. methyl alcohol and water, give a conductivity considerably less than the conductivity of these salts in either pure alcohol or water. Cohen[2] gives similar results with ethyl alcohol and water, and finds that potassium iodide in 80 per cent. alcohol shows a larger conductivity below $V = 512$ than in pure alcohol, but at a greater dilution the conductivity is less in the mixed solvents than it is in either of the pure solvents. Wakeman,[3] working with mixtures of ethyl alcohol and water, found that the equation,

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[1] Phil. Mag., **24**, 378 (1893).

[2] Wied. Ann., **33**, 58 (1888); **43**, 838 (1891).

[3] Charcow, 1892.

[4] Beibl., Wied. Ann., **9**, 131 (1885).

[5] *Ibid.*, **18**, 219, 365 (1894).

[6] Wied. Ann., **52**, 328 (1894).

[7] *Ibid.*, **50**, 263 (1893).

[8] Gazz. Chim. Ital., [1] **26**, 119 (1896).

[9] Z. physik. Chem., **5**, 35 (1890).

[10] Compt. rend., **125** 240 (1897).

[11] Bull. Soc. Chim., [3] **19**, 321 (1897).

[12] Z. physik. Chem., **4**, 432 (1889).

[13] Wied. Ann., **52**, 328 (1894).

[14] J. Phys. Chem., **3**, 26 (1899).

[15] Z. physik. Chem., **11**, 49 (1893).

$$\frac{\Delta}{p(100-p)} = \text{constant}$$

held for many substances in mixtures of the above-named solvents (Δ is the difference between the conductivity of the electrolyte in water and in the mixture, and p the percentage of alcohol by volume).

From his own and from Wakeman's observations Cohen points out the following relation:

$$\frac{\mu_v \, H_2O}{\mu_v \, H_2O.Alc.} = \text{constant.}$$

This relation holds independently of temperature and concentration. He remarks that either the dissociation of the salt with which he worked is the same or that in these mixtures conductivity is not a direct measure of dissociation. Roth later found that the relation given by Wakeman holds, while that given by Cohen does not.

Jones[4] and his coworkers have done a fairly large amount of work on conductivity and viscosity in mixed solvents. Since the following is essentially a continuation of that work a very brief review of the latter is necessary.

[1] Z. physik. Chem., **21**, 35 (1896).

[2] *Ibid.*, **25**, 31 (1898).

[3] *Ibid.*, **11**, 49 (1893).

[4] Publication No. **80**, Carnegie Institute.

Jones and Lindsay[1] found that the phenomenon discovered by Zelinski and Krapiwin is not confined to a few salts in mixtures of methyl alcohol and water only, but that it holds over a large range of salts and also in ethyl alcohol-water mixtures. It holds less generally at 25° than at 0°, and in ethyl alcohol-water mixtures less than in methyl alcohol-water mixtures. The conductivities were always less than the mean calculated from the conductivities in the pure solvents.

As a partial explanation they advance the following tentative suggestion: According to the theory of Dutoit and Aston only the polymerized molecules of the solvent dissociate the molecules of the solute. It is well known that water and the alcohols used are highly associated substances. On coming into contact with each other, they break down the association of each other until equilibrium is reached; and, consequently, they have less dissociating power. In methyl alcohol-water mixtures where association of the constituents is greatest the dissociation is greatest. Other facts are in accordance with this suggestion. Since at the lower temperatures the association is greatest in the constituents, we would expect the greatest abnormality here. And such is the case.

These conclusions were subsequently further confirmed by the cryoscopic work of Jones and Murray.[2] They worked with water and formic and acetic acids, and determined the molecular weights of each in the other by the freezing-point method. They found that the molecular weights of these substances are always less than the molecular weights of the pure substances as determined by the method of Ramsay and Shields. They thus conclude that the action of an associated solvent upon another associated solvent is analogous to the action of an associated solvent upon an electrolyte.

Jones and Carroll[3] extended the work of Jones and Lindsay. They worked with both binary and ternary electrolytes. As solvents they used methyl and ethyl alcohols and mixtures of these two. Acetic acid was also used. In mixed solvents a minimum was found with the following salts: cadmium iodide, sodium iodide, and hydrochloric acid in mixtures of ethyl alcohol and water. That of cadmium iodide exists for dilutions up to 50 only, at 0°; beyond that there is no minimum. At 25° there is no minimum.

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[1] THIS JOURNAL, **28**, 329 (1902). Z. physik. Chem., **56**, 129 (1906).

[2] THIS JOURNAL, **30**, 193 (1903).

[3] *Ibid.*, **32**, 521 (1904).

Somewhat surprising results were found with hydrochloric acid in methyl alcohol and water mixtures; μ_∞ occurs at very low dilutions in mixtures containing up to 90 per cent. alcohol (between V 100 and V 200), while in 100 per cent. methyl alcohol it is not found even as high as V 2104. In the dilutions above these limiting values there is a decrease in conductivity.

The relation pointed out by Wakeman,

$$\frac{\Delta}{p(100-p)} = \text{constant},$$

does not hold; neither does that of Cohen.

They explain the cause of the minimum as follows: There are two factors which determine conductivity, the amount of dissociation and ionic mobility. Decrease or increase of either of these produces a corresponding result in the conductivity.

They point out that there is a close connection between the fluidity and conductivity of a solution. These vary directly. When the solutions are brought together there is an increase in viscosity, or decrease in fluidity, which is its reciprocal. Consequently, the ions are much retarded in their movements and the conductivity diminished. As the temperature rises there is a shifting of the minima towards that mixture containing the greatest percentage of alcohol. In this shifting, however, the fluidity minima, they state, lag behind the conductivity minima.

They propose the following hypothesis: "The conductivities of comparable equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohol, other alcohols of the same series, acetone, etc.) are inversely proportional to the coefficients of viscosity of the solvent in question, and directly proportional to the association factor of the solvent in question." These conclusions may be formulated as follows:

$$\frac{\mu_v}{x} = \text{constant, or } \frac{\mu_v \eta}{a} = \text{constant.}$$

The work of Jones and Bassett[1] with silver nitrate in both methyl alcohol-water and ethyl alcohol-water mixtures deals with the same phenomena as were previously discussed. There are well marked minima in the curves at both 0° and 25° in methyl alcohol-water mixtures, but no such minima occur in ethyl alcohol-water mixtures. In all cases, however, the curves fall much below the straight line of averages.

Jones and Bingham[2] measured the conductivities of lithium nitrate, potassium iodide, and calcium nitrate in water, methyl and ethyl alcohols and acetone, and binary mixtures of these solvents. They also made a large number of viscosity measurements of pure solvents, of mixed solvents, and of electrolytes in solution. In acetone and water mixtures the same minima which previous workers had observed were also observed. While the conductivity minima are intimately related to the minima of fluidity, the conductivity curves of different salts show marked differences. In acetone and alcohol mixtures the curves conform to the law of averages, that is, the conductivity curves are nearly straight lines. From this fact they conclude that the mixtures do not form more complex molecular aggregations.

A peculiar fact, and one not previously known, was here discovered. Lithium and calcium nitrates in mixtures of acetone with methyl or ethyl alcohol present a very pronounced maximum of conduction. This must be due to one of two causes: There is either an increase in dissociation and, consequently, an increase in the number of ions present, or there must be a diminution in the size of the ionic spheres, causing them to move more rapidly. We eliminate the first cause since fluidities of mixtures of acetone and the alcohols obey the rule of averages. This would indicate that there is no increase in the molecular aggregation in these mixtures, and according to Dutoit and Aston's hypothesis such a mixture would not dissociate to a greater extent than the constituent solvents. Since we can eliminate increased dissociation as the cause of the maximum, it must be due to the change in the dimensions of the ionic spheres. The previous work of Dutoit and Friederich and of Jones and Carroll is incomplete since it does not take into consideration the size of the ionic spheres.

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[1] This Journal, **32**, 409 (1904).

[2] *Ibid.*, **34**, 481 (1905).

The tendency to show maxima in conductivity increases from potassium iodide through calcium nitrate to lithium nitrate, which seem to show these effects most strongly. This may be connected with the ionic velocities, since potassium is a small ion and a comparatively rapidly moving one, and lithium forms, by combination with the solvent, a large ion and one that moves more slowly.

Jones and Rouiller[1] worked with silver nitrate in the solvents used by Jones and Bingham. In a general way they found results similar to those previously obtained. There is a striking similarity in the curves at 0° and 25° in mixtures of ethyl alcohol and acetone. There is a pronounced maximum at both 0° and 25° in the 25 per cent. acetone mixture in the more concentrated solutions, and shifting with increase in dilution through the 50 per cent. mixture to the 75 per cent. mixture. For pure acetone these curves decline rapidly. For mixtures of methyl and ethyl alcohols, the curves are nearly straight lines following the fluidity curves.

Jones and McMaster[2] worked with lithium bromide and cobalt chloride in the same solvents that had been employed by Bingham. The fluidities of water, methyl alcohol, ethyl alcohol, and acetone, and binary mixtures of these solvents were measured. The conductivities of these mixtures with water show a well-marked minimum. This minimum shows an intimate relation to that of fluidity. Lithium bromide in mixtures of methyl and ethyl alcohols gives no minimum in conductivity. The curves are nearly straight lines, except at the higher concentrations where there is a slight sagging at both temperatures. The same salt shows a maximum in conductivity in acetone-methyl alcohol mixtures with 75 per cent. acetone. The maxima increase with rise in temperature. In acetone-ethyl alcohol mixtures the same characteristics are manifested.

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[1] THIS JOURNAL, **36**, 42 (1906).

[2] *Ibid.*, **36**, 325 (1906).

Cobalt chloride in methyl alcohol-water mixtures shows minima at both temperatures. At the higher temperature the minimum is most marked with 75 per cent. alcohol. In mixtures of ethyl alcohol and water, this salt shows a point of inflection at both temperatures and at all dilutions. These results are similar to those obtained by Jones and Bingham with calcium nitrate in acetone-water mixtures. In ethyl alcohol-methyl alcohol mixtures there is no distinct minimum but a sagging of the curve.

The minimum of fluidity corresponds to that of conductivity. There is in both methyl alcohol-water and ethyl alcohol-water mixtures a tendency of the minimum to shift towards the mixture containing the greatest percentage of alcohol whenever there is a rise in temperature. The authors reach the conclusion suggested by former workers that a diminution in the fluidity of the solvent, which would bring about a corresponding decrease in ionic mobility, is an important factor in causing the minimum in conductivity; and that the change in the size of the ionic spheres or the atmosphere which surrounds the ions should also be taken into account.

Several points in connection with the temperature coefficients are important. In nearly every case the temperature coefficients are smaller in the more concentrated solutions. Jones had already explained the phenomena in the following manner: In practically all solutions there is combination between solvent and solute. As dilution increases the solvates become more complex. Change in temperature affects most greatly the complex solvates, therefore we should expect the largest temperature coefficients at high dilutions.

At certain concentrations in methyl alcohol and acetone a negative temperature coefficient manifests itself. Conductivity varies directly as dissociation and fluidity. Since rise in temperature diminishes dissociation, and increases fluidity, it would seem that there would be a point where these two influences would equalize each other, and the temperature coefficient become zero. This concentration is reached at V 200 in a 75 per cent. acetone and methyl alcohol mixture. Beyond this dilution there is a negative temperature coefficient.

Jones and Veazey[1] measured the conductivities and viscosities of solutions of copper chloride and potassium sulphocyanate in water, methyl alcohol, ethyl alcohol and acetone, and binary mixtures of these solvents. The minimum which was previously observed with different electrolytes is here also observed in some cases. This minimum is more pronounced at the higher dilutions. Where no minimum occurs there is a decided fall below the average value for the pure solvents. There is an interesting difference in the values for molecular conductivity in the pure solvent with increasing dilutions. In pure water, copper chloride, a ternary electrolyte, shows a much greater conductivity than potassium sulphocyanate, a binary electrolyte. In pure methyl alcohol the opposite condition exists. The conductivity of potassium sulphocyanate is the greater. This fact appears in previous work. Ethyl alcohol shows the same phenomenon.

The temperature coefficients of conductivity increase with increase in dilution. There is one exception—cobalt chloride in methyl alcohol. A marked negative temperature coefficient of viscosity is shown by potassium sulphocyanate in aqueous solutions.

In a recent communication Jones and Veazey[2] report the results of a study of solutions of tetraethylammonium iodide in mixtures of water, the alcohols and nitrobenzene. In mixtures of the alcohols and water there is a well-defined minimum in conductivity. In mixtures of the alcohols with each other there is no minimum, although the curves fall below the averages. In methyl alcohol and nitrobenzene the same phenomena occur, but in ethyl alcohol and nitrobenzene there is a maximum. The conductivity curves correspond very well with the fluidity curves.

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[1] This Journal, **37**, 405 (1907). Z. physik. Chem., **61**, 41 (1908).
[2] This Journal, **41**, 433 (1909).

Jones and Mahin[1] took up the study of cadmium iodide and lithium nitrate in binary mixtures of water, methyl and ethyl alcohols and acetone, and lithium nitrate in ternary mixtures of these solvents. Viscosity measurements of these solutions were also made. These measurements were carried to as high dilutions as possible—in some cases as high as 200,000 liters. At these high dilutions it was impossible to prevent considerable error due to the large correction for the specific conductivities of the solvents, and the large cell constants. With lithium nitrate the product of viscosity and molecular conductivity is nearly a constant for mixtures of acetone with methyl alcohol and ethyl alcohol. This value is independent of the temperature. The value is nearly 0.70, which is Walden's value for tetraethylammonium iodide. With acetone-water mixtures the product varies between 1.00, the value for water, and 0.63, the value for acetone.

Interesting results were obtained by determining the molecular weights of lithium nitrate in acetone by the boiling-point method. The object was to test the assumption that the low conductivity of this salt in ordinary solutions is due to the association of the salt. In the most dilute solution—0.09 normal—which could be determined accurately, the boiling-point method showed a molecular weight of 83.1, while the normal molecular weight is 69.07. We can, therefore, conclude that there is association, and this would account for the low conductivity in solutions at great dilutions.

Jones had already shown that cadmium iodide in acetone is associated. This salt was next investigated and found to behave like lithium nitrate in its molecular conductivity. There is an irregularity in the product of conductivity and viscosity in acetone and methyl alcohol mixtures, while in the pure solvents these products are nearly the same. In acetone-ethyl alcohol mixtures there is a fair degree of constancy in these products. Jones has shown that there is considerable polymerization of cadmium iodide in acetone.

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[1] Z. physik. Chem., **62**, 41 (1908).

Conductivity and viscosity in ternary mixtures of the above solvents were next taken up, and a considerable amount of work was done. The object was to determine whether any essentially new pricinples could be discovered by increasing the number of components in the solvent mixture. The results are about what we would expect from a knowledge of the behavior of solutions in binary solvent mixtures.

Turner,[1] working in Jones's laboratory, made various conductivity measurements of potassium iodide, lithium chloride and lithium bromide in pure ethyl alcohol, at high dilutions. Many precautions were pointed out which were very helpful in the present work. The purification of solvents, precautions necessary to prevent contact with foreign substances, and other sources of error were investigated and discussed in detail. After repeated experiments it was found that small traces (0.2 to 0.3 per cent.) of water do not appreciably affect the conductivity.

The conductivity of potassium iodide in ethyl alcohol was measured up to a dilution of 450,000 liters. A maximum of molecular conductivity of 48.5 was reached at about 20,000 liters. From this the ionization was calculated. Measurements of conductivity were made at as high as 78°. The temperature coefficients increase with increasing temperatures and with increasing dilution. Ionization decreases considerably with rise in temperature. A 0.1 normal solution is dissociated 49 per cent. at 0°, 46 per cent. at 25° and about 35 per cent. at the boiling point of ethyl alcohol.

Determinations of ionization were also made by the boiling-point method, but these are in all cases considerably lower than those obtained by the conductivity method.

The work of Jones and Schmidt[4] introduces a new solvent, *glycerol*. They measured the conductivity and viscosity of lithium bromide, cobalt chloride, and potassium iodide in glycerol, methyl and ethyl alcohols, and binary mixtures of these and water. Glycerol was employed as a solvent because of its high viscosity. Its dielectric constant is about one-fifth that of water and it ought to have a fairly high dissociating power. It has remarkable solvent properties. But little work had previously been done with glycerol as a solvent. For measuring viscosity a viscometer with especially large bore had to be constructed.

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[1] This Journal, **40**, 558 (1908).

[2] This Journal, **42**, 37 (1909).

Measurements of conductivity were made at 25°, 35° and 45°. Lithium bromide in mixtures of glycerol with water, methyl alcohol, and ethyl alcohol shows no minimum, but there is a wide departure from the law of averages, and a marked sagging in the curves. We would hardly expect a minimum since there is probably no mixture of glycerol with these other solvents which is more viscous than glycerol itself.

With cobalt chloride the conductivities in pure glycerol increase regularly. The conductivity values are considerably higher than the corresponding values for lithium bromide. Since cobalt chloride is a ternary electrolyte and lithium bromide a binary one, these results are just what we should expect. In pure ethyl alcohol, however, the case is different. The values for the conductivity of cobalt chloride are abnormally low. Lithium bromide, for instance, in a 0.1 N solution has a molecular conductivity of 15.8 at 25°. We should expect that cobalt chloride, since it is a ternary electrolyte, would have a conductivity probably 50 per cent. greater, but the value for the molecular conductivity of cobalt chloride in ethyl alcohol at the above concentration is only 4.71. Many of the halides of the heavy metals tend to form complexes when dissolved in organic solvents. It was supposed that the low conductivity of cobalt chloride in ethyl alcohol, at least in the more concentrated solutions, was due to polymerization of the molecules. Molecular weight determinations of cobalt chloride in ethyl alcohol were made by the boiling-point method. The mean of three determinations is 140 at about one-twelfth normal concentration, while the molecular weight for the compound $CoCl_2$ is 129.9. This would seem to indicate that there is association and, consequently, a lower conductivity than would be expected.

Potassium iodide in glycerol behaves like the other salts. There is a slight increase in conductivity with dilution. In each case the conductivities for mixed solvents are less than the average for pure solvents.

A new feature is the magnitude of the temperature coefficients of conductivity. Some are almost as high as nine per cent. Cobalt chloride in ethyl alcohol manifests a negative temperature coefficient. A negative viscosity manifests itself in the case of potassium iodide in water, and in 25 per cent. and 50 per cent. glycerol and water at both 25° and 35°.

An elaborate investigation has been carried out in this laboratory during the past year by Guy on glycerol as a solvent. The results of this work will soon be published.

EXPERIMENTAL.

This investigation was undertaken for the purpose of obtaining facts by means of which the following questions might be answered:

1. At what dilutions do the maxima in conductivity occur for various salts in methyl and ethyl alcohols?

2. Is there any relation between these maxima in conductivity for different salts in different solvents?

3. What is the magnitude of the dissociation of these salts in these solvents as calculated by means of the maxima in conductivity?

4. What relation does this dissociation bear to that found by means of the boiling-point method?

Apparatus.

The Kohlrausch method was used. The wire was calibrated and was found to be of uniform thickness throughout.

The cells were of the latest type used in this laboratory. They were devised for measuring the conductivity of very dilute solutions where there is great resistance. They consist of two concentric platinum cylinders so placed one within the other that the electrodes are only about 1 mm. apart. They are held together by means of small drops of fusion glass placed between them. These electrodes have a surface of about 48.75 square cm. One of these cells had a constant as low as 2.82. The vertical position of the electrodes permitted the ready escape of all air bubbles, neither were they difficult to wash and dry if the proper precautions were observed. These cells gave excellent results, and a sharp minimum was obtained upon the bridge without difficulty. The constants were determined by means of 0.01 N and 0.001 N solutions of potassium chloride. These constants were frequently redetermined but were found to change but little throughout the work.

All the appparatus was carefully calibrated. The necessary precautions concerning temperature were observed. The temperature in the 25° bath was regulated with a sensitive thermometer calibrated against a German Reichanstalt thermometer. The 0° bath was from time to time tested to see that there was no change in temperature. At no time were measurements made when the temperature varied more than 0°.04 from that required. Careful tests were made to find the time required for the temperature of the solutions within the cells, both at 0° and 25°, to reach an equilibrium. This equilibrium was indicated by a constant conductivity. In all cases nearly an hour was necessary. Three readings were always taken and the mean was employed.

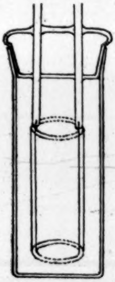

Fig. I.—Type of cell employed in this work.

For 0° measurements a battery jar filled with ice and water was placed within a bucket and surrounded with ice and water. The cells were placed in the battery jar and covered with glass. Ample time was allowed for the temperature to reach an equilibrium. Frequently the first reading was repeated after an interval of fifteen minutes or more, insuring equilibrium.

Extreme precautions were necessary in washing the apparatus. No fumes were permitted in the room. Immediately before using, the cells and flasks were thoroughly washed with distilled water, then rinsed several times with conductivity water and finally washed repeatedly with alcohol. This alcohol was always kept pure and used only a few times before it was dried and redistilled. Ether was not employed in drying since there is danger of fats being contained in it. The apparatus was then carefully dried. Before a solution was made up in a flask the latter was rinsed with a portion of the solvent, and the cell was rinsed with a portion of the solution. In many cases of very dilute solutions the flask in which the solution was to be made up was first cleaned, dried and rinsed with alcohol, the conductivity of this alcohol determined, and this same alcohol was employed to dilute the solution and its conductivity was used for the correction for the specific conductivity of the solvent. As a rule, there was little change in this conductivity when the above precautions were observed, and yet, because of the large volume, this change was at times quite appreciable.

Salts.

The salts used were potassium iodide, ammonium bromide, potassium sulphocyanate, lithium nitrate, sodium iodide, copper chloride, calcium nitrate and cobalt chloride.

In all cases the necessary precautions were observed in purifying the salts, Kahlbaum's best products being employed. All were recrystallized a number of times, finally from conductivity water and some from absolute alcohol. All were dried at a temperature of 125°–150°. Those which are very deliquescent were heated for a long time, some for several days, in an air bath. Those chlorides which readily form oxychlorides when heated in the air were recrystallized several times, then dried in a vacuum desiccator over sulphuric acid for several days, and finally heated for a long time in a current of dry hydrochloric acid gas. They were then placed in a desiccator over sulphuric acid and potassium hydroxide for several days. All other salts but the latter class were dried to constant weight before making up each solution.

Solvents.

The solvents used were methyl and ethyl alcohols and mixtures of these with water. Considerable difficulty was experienced in purifying methyl alcohol so as to obtain it with as low a specific conductivity as possible. This low conductivity was important since there was danger of introducing considerable error due to the large correction for the specific conductivity of the solvent at these high dilutions. It was evident from the results that some foreign substance was contained in the methyl alcohol which it was difficult to remove. It was supposed that this unusually high conductivity was due probably to pyridine bases, and that these might be removed by treatment with sulphuric acid. The cold alcohol was treated with a small quantity of dilute sulphuric acid. It was then distilled, the first runnings being always discarded, and the receiver removed while a considerable quantity was still in the flask. The alcohol was then boiled with lime for a day and distilled. In some cases it was repeatedly treated with lime and repeatedly distilled. One quantity thus treated gave a conductivity as low as 7.1×10^{-7}. On standing, however, the conductivity changed somewhat, so that not all work was done with alcohol having quite such low conductivity.

The ethyl alcohol was distilled from lime several times, then repeatedly distilled until it had a conductivity of about 2.6×10^{-7}. The water was purified by the method of Jones and Mackay.

Solutions.

All solutions were made by direct weighing. In those cases where the solutions were to be very dilute and but a small quantity of the salt was needed, a 0.1 N solution was made as a mother solution. This was then diluted to a second mother solution. From this the final dilutions were made directly. Only in a few cases was a final dilution made from any other but the first or the second mother solution.

All solutions were made up at 20°. Enough time was always allowed for the temperature to come to equilibrium. The solutions when once placed in the cells were not removed from them until after measurements were made for both temperatures. They were never left in the cells longer than necessary because of possible decomposition:

Table I.—Conductivity of Potassium Iodide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	69.05	96.18	0.01572
2048	70.62	99.22	0.01620
4096	71.48	101.14	0.01660
8192	72.13	102.4	0.01679
16384	74.5	104.8	0.01627
32768	76.6	107.2	0.01598

Table II.—Conductivity of Potassium Iodide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	23.4	36.4	0.02222
2048	28.6	44.9	0.02280
4096	29.4	47.2	0.02422
8192	32.7	47.5	0.01810
16584	32.5	47.4	0.01834
33168	32.0	47.2	0.01900

Table III.—Conductivity of Ammonium Bromide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	66.1	93.1	0.01634
2048	69.9	94.1	0.01377
4096	70.6	96.7	0.01482
8129	71.8	96.8	0.01393
16584	69.2	94.9	0.01485

Table IV.—Conductivity of Ammonium Bromide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1024	32.1	37.0	0.02047
4096	25.2	39.6	0.02285
16384	27.5	39.1	0.01687
65536	29.8	39.5	0.01302

Table V.—Conductivity of Potassium Sulphocyanate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	69.1	98.3	0.01690
3200	71.1	101.0	0.01682
12800	73.0	103.7	0.01682
25600	83.5	106.3	0.01092

Table VI.—Conductivity of Potassium Sulphocyanate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	28.2	43.8	0.02218
3200	28.6	45.7	0.02391
6400	29.2	46.67	0.02393
12800	29.23	45.4	0.02213
25600	28.57	43.64	0.02110

Table VII.—Conductivity of Lithium Nitrate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	58.83	83.24	0.01659
3200	59.89	85.98	0.01743
6400	61.46	89.29	0.01811
12800	59.69	91.35	0.02121
25600	60.36	93.61	0.02203

Table VIII.—Conductivity of Lithium Nitrate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	23.82	36.67	0.02157
3200	24.13	38.44	0.02372
6400	25.63	40.87	0.02378
12800	25.87	40.02	0.02187
25600	...	43.30	0.00000

Table IX.—Conductivity of Sodium Iodide in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
512	60.32	87.67	0.01814
1024	64.15	90.91	0.01669
2048	63.65	91.93	0.01777
4096	63.34	91.06	0.02382
8192	65.90	93.40	0.01669
16384	63.1	91.8	0.01819

Table X.—Conductivity of Sodium Iodide in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
512	24.41	38.06	0.02237
1024	25.12	39.66	0.02315
2048	25.89	40.92	0.02322
4096	26.89	41.84	0.02224
8192	26.06	42.86	0.02579
16384	26.79	42.02	0.02274
32768	28.83	43.22	0.01996

Table XI.—Conductivity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	83.53	106.04	0.01078
3200	93.50	120.58	0.01156
6400	105.46	138.46	0.01252
12800	112.52	151.73	0.01394
25600	119.44	164.6	0.01509
51200	124.58	175.0	0.01620

Table XII.—Conductivity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	17.19	24.48	0.01696
3200	19.11	29.52	0.02179
6400	21.45	34.16	0.02370
12800	24.22	39.23	0.02537
25600	27.61	45.67	0.02616
51200	31.92	51.62	0.02469

Table XIII.—Conductivity of Cobalt Chloride in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	101.94	138.58	0.01438
3200	110.98	152.34	0.01878
6400	115.76	162.38	0.01612
12800	116.22	165.74	0.01704
25600	115.34	166.08	0.01760
51200	112.58	157.96	0.01614

Table XIV.—Conductivity of Cobalt Chloride in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	19.99	25.61	0.01125
3200	22.75	30.13	0.01298
6400	25.68	34.15	0.01319
12800	29.25	39.01	0.01335
25600	31.36	43.62	0.01564
51200	31.62	46.31	0.01858
102400	28.42	(52.26)	0.00000

Table XV.—Conductivity of Copper Chloride in Methyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	64.13	78.58	0.09013
3200	75.43	89.31	0.07361
6400	85.22	101.28	0.07538
12800	91.3	112.3	0.09201
25600	90.5	116.4	0.01145
51200	79.1	112.1	0.01669

Table XVI.—Conductivity of Copper Chloride in Ethyl Alcohol at 0° and 25°.

V.	0°.	25°.	Temperature coefficients.
1600	16.08	20.96	0.01214
3200	18.94	25.74	0.01436
6400	21.06	30.70	0.01831
12800	22.52	34.16	0.02067
25600	22.94	37.79	0.02589

Table XVII.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	45.03	90.44	0.04023
2048	44.26	91.60	0.04278
4096	45.60	92.80	0.04140
8192	45.56	92.40	0.04112
16384	48.60	96.0	0.04000
32768	51.99	100.7	0.04517

Table XVIII.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	35.77	72.24	0.04078
2048	36.07	73.37	0.04137
4096	37.49	74.64	0.03968
8192	38.04	76.20	0.04013
16384	40.18	79.9	0.03945
36768	46.86	93.1	0.03948

Table XIX.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	41.63	71.37	0.04952
2048	41.20	72.00	0.05064
4096	41.82	73.19	0.05247
8192	44.98	75.41	0.05475
16384	46.83	75.3	0.05339
32768	49.95	71.8	0.01910

Table XX.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	32.38	74.80	0.05241
2048	32.75	76.23	0.05311
4096	32.73	76.60	0.05361
8192	33.88	77.20	0.05115
16584	35.30	80.3	0.05138
33168	39.88	86.8	0.04702

Table XXI.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	20.04	52.12	0.06401
2048	20.92	52.83	0.06073
4096	21.28	53.20	0.06000
8192	21.34	54.09	0.06120
16384	20.94	55.23	0.06550
32768	23.10	59.16	0.06244

Table XXII.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1024	20.58	44.14	0.04579
2048	21.39	45.04	0.04423
4096	21.50	45.91	0.04541
8192	21.34	45.96	0.04615
16384	21.85	47.85	0.04760
32768	23.68	51.04	0.04491
65536	25.11	53.30	0.04491

Table XXIII.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	66.85	144.1	0.04620
3200	68.20	148.5	0.04831
6400	69.39	151.8	0.04749
12800	70.50	152.3	0.04641
25600	72.08	159.0	0.04823
51200	80.30	181.6	0.05046

Table XXIV.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	53.94	113.5	0.04417
3200	55.84	115.7	0.04287
6400	56.59	119.4	0.04440
12800	57.86	122.3	0.04456
25600	58.70	124.1	0.04457
51200	65.2	138.6	0.04503

Table XXV.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent. Methyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	56.23	101.5	0.03220
3200	63.32	115.4	0.03290
6400	64.22	118.1	0.03356
12800	66.48	120.7	0.03262
25600	66.2	122.3	0.03390
51200	69.0	124.9	0.03241

Table XXVI.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	47.92	119.7	0.05992
3200	49.08	123.6	0.06072
6400	50.80	127.4	0.06032
12800	50.73	129.7	0.06227
25600	51.83	135.0	0.06419
51200	57.74	154.4	0.06697
162400	60.20	170.5	0.07327

Table XXVII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	31.16	81.56	0.06469
3200	32.27	84.67	0.06495
6400	32.70	86.56	0.06588
12800	33.70	88.28	0.06479
25600	33.25	87.42	0.06517
51200	34.18	90.8	0.07743
102400	34.40	89.7	0.07609

Table XXVIII.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent. Ethyl Alcohol and Water.

V.	0°.	25°.	Temperature coefficients.
1600	31.0	67.1	0.04658
3200	32.4	70.5	0.04704
6400	33.1	73.4	0.04870
12800	33.7	74.6	0.04855
25600	34.4	74.8	0.04698
51200	34.0	72.4	0.04518

Table XXIX.—Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	87.9	45.0*	35.8	41.6*	69.1
2048	88.5	44.3	36.1	41.2	70.6*
4096	88.9	45.6	37.5	41.8	71.5
8192	89.2*	46.6	38.0*	45.0	72.1
16384	89.2	46.6	40.2	46.8	74.5
32768	89.2	52.0	46.9	49.9	76.6

Table XXX.—Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 25°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	135.6	90.4	72.2	71.4	96.2
2048	136.2	91.6	73.4	72.0	99.2
4096	136.7	92.8*	74.7	73.2	101.1
8192	136.9*	92.4	76.2	75.4*	102.4
16584	136.9	95.3	79.9	75.3	104.8
33168	136.9	100.7	93.1	71.8	107.2

Table XXXI.—Conductivity of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	87.9	32.4	20.0	20.6	23.4
2048	88.5	32.8*	20.9	21.4	28.6
4096	88.9	32.7	21.3*	21.5*	29.4
8192	89.2*	33.9	21.3	21.3	32.7*
16584	89.2	35.3	20.9	21.8	32.5
33168	89.2	39.9	23.1	23.7	32.0
65536	....	....	....	25.1	....

Table XXXII.—Conductivity of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 25°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	135.6	74.1	52.1	44.1	36.4
2048	136.2	76.2	52.8	45.0	44.9
4096	136.7*	76.6	53.2	45.9	47.2
8192	136.9	77.2	54.1	46.0*	47.5
16584	136.9	80.3	55.2	47.9	47.4*
33168	136.9	86.8	59.2	51.0	47.2

Table XXXIII.—Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	66.9	53.9	56.2	101.9
3200	68.2	55.8	63.3	111.0
6400	69.4	56.6	64.2	115.8
12800	75.5*	57.9	66.5*	116.2*
25600	72.1	58.7	66.2	115.3
51200	80.3	65.2	69.0	112.6

Table XXXIV.—Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 25°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	144.1	113.5	101.5	138.58
3200	148.5	115.7	115.4	152.34
6400	151.8	119.4	118.1	162.38
12800	152.3	122.3	120.7	165.74
25600	159.0	124.1	122.3	166.1
51200	181.6	136.6	124.9	158.0

Table XXXV.—Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	47.92	31.16	31.0	19.99
3200	49.08	32.27	32.4	22.75
6400	50.80*	32.70	33.1	25.68
12800	50.73	33.70*	33.7	29.25
25600	51.83	33.25	34.4*	31.36
51200	57.74	34.18	34.0	31.62*
162400	60.20	34.40	....	28.42

Table XXXVI.—Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 25°.

V.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	119.7	81.56	67.1	25.61
3200	123.6	84.67	70.5	30.13
6400	127.4	86.56	73.4	34.15
12800	129.7	88.28	74.6	39.01
25600	135.0	87.42	74.8	43.62
51200	154.4	90.8	72.4	46.31

Table XXXVII.—Dissociation of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	98.4	100.0	94.2	100.0	97.8
2048	99.2	...	95.0	...	100.0
4096	100.0	...	98.7	...	...
8192	...	...	100.0	...	...

Table XXXVIII.—Dissociation of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1024	98.4	98.7	93.9	95.8	71.5
2048	99.2	100.0	98.1	99.5	87.4
4096	100.0	100.0	100.0	100.0	90.0
8192	...	...	...	...	100.0

Table XXXIX.—Dissociation of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

V:	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	100.0	88.6	...	84.5	87.6
3200	...	90.3	...	95.1	95.5
6400	...	91.9	...	96.5	99.6
12800	...	100.0	...	100.0	100.0

Table XL.—Dissociation of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

V.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
1600	100.0	94.2	92.5	93.0	63.2
3200	...	96.6	95.7	94.1	72.0
6400	...	100.0	97.0	96.2	81.2
12800	...	...	100.0	97.9	92.5
25600	...	...	...	100.0	92.2
51200	...	...	...	...	100.0

Table XLI.—Maxima in Molecular Conductivity for Certain Salts in Pure Alcohols.

	0°.	25°.
KI in methyl alcohol	(77.5)	(112.6)
KI in ethyl alcohol	32.7	47.5
NH_4Br in methyl alcohol	71.8	96.8
NH_4Br in ethyl alcohol	(30.3)	39.6
KCNS in methyl alcohol	(69.2)	(110.4)
KCNS in ethyl alcohol	29.2	46.7
$LiNO_3$ in methyl alcohol	61.5	(96.7)
$LiNO_3$ in ethyl alcohol	25.9	40.8
NaI in methyl alcohol	64.1	91.9
NaI in ethyl alcohol	27.0	42.8
$CuCl_2$ in methyl alcohol	91.3	116.4
$CuCl_2$ in ethyl alcohol	(25.7)	(32.7)
$Ca(NO_3)_2$ in methyl alcohol	....	....
$Ca(NO_3)_2$ in ethyl alcohol	....	....
$CoCl_2$ in methyl alcohol	116.2	166.0
$CoCl_2$ in ethyl alcohol	31.6	(46.7)

Boiling-Point Data.

Table XLII.—Sodium Iodide in Methyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
53.949	2.8131	0.03478	0.429	12.33	46.8
55.352	2.7357	0.03300	0.425	12.90	53.6
61.195	2.5597	0.02790	0.3556	12.74	51.8
52.842	2.1082	0.02661	0.347	13.04	55.2
57.480	2.2060	0.02560	0.318	12.42	47.8
55.686	1.7227	0.02108	0.263	12.50	48.8
54.510	1.8380	0.02268	0.298	13.14	56.4
59.798	1.8080	0.02005	0.251	12.52	49.0
55.546	1.1943	0.01421	0.178	12.52	49.0
53.215	0.9665	0.01211	0.155	12.80	52.4

Table XLIII.—Sodium Iodide in Ethyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
53.100	3.1715	0.03984	0.585	14.63	27.7
54.734	2.7683	0.03374	0.512	15.17	31.9
64.744	3.2084	0.03303	0.495	14.98	30.2
53.896	2.6133	0.03235	0.481	14.87	29.3
61.293	2.5117	0.02730	0.402	14.73	28.0
55.509	2.0431	0.02455	0.365	14.86	29.1
61.701	2.1323	0.02306	0.351	15.22	32.3
59.294	1.9686	0.02214	0.327	14.76	28.3
54.368	1.5300	0.01877	0.281	14.97	30.1
64.926	1.4171	0.01455	0.223	15.32	33.2

Table XLIV.—Calcium Nitrate in Methyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
56.762	1.4954	0.01685	0.160	9.969	9.5
64.823	1.2154	0.01142	0.107	9.366	8.6
52.567	0.9792	0.01135	0.106	9.340	6.8
63.825	1.2489	0.01131	0.110	9.725	7.9
62.275	0.7453	0.00729	0.073	10.009	9.3

Table XLV.—Calcium Nitrate in Ethyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
50.476	1.1004	0.01328	12.68	0.168	5.1
54.301	1.3570	0.01228	12.86	1.158	5.9
52.355	0.6795	0.00791	12.51	0.099	4.4

Table XLVI.—Cadmium Iodide in Ethyl Alcohol.

Solvent.	Salt.	Concentration.	Rise.	Molecular rise.	Dissociation.
48.831	3.5915	0.02007	0.253	12.60	4.8
54.657	3.6962	0.01850	0.230	12.43	4.05
50.956	3.1632	0.01694	0.214	12.63	4.9
51.574	2.9277	0.01549	0.195	12.58	4.7
52.348	2.7683	0.01443	0.181	12.57	4.6
52.316	2.6784	0.01397	0.176	12.58	4.6
48.034	2.1137	0.01201	0.152	12.67	5.0
51.668	1.2491	0.00660	0.082	12.42	4.0
56.563	0.8712	0.04204	0.052	12.38	4.3

DISCUSSION OF RESULTS.

Tables I to XVI show the conductivity of the various salts worked with in the pure solvents at both 0° and 25°. Nine of these tables show a maximum either at one or both temperatures. The other tables show no maximum up to the highest dilutions measured. In several cases maxima occur at one temperature and none at the other. In some tables the maxima occur at the same concentration at both temperatures; in others at different concentrations, but they always occur at concentrations which are close together. The temperature coefficients in general agree very well. Nearly all show a slight increase with increasing dilution.

Tables XVII to XXVIII show the conductivity of potassium iodide and cobalt chloride in mixtures of methyl alcohol and water at both 0° and 25°. In some of these tables the maximum conductivities are reached. The maxima generally occur at a greater concentration at 0° than at 25°. In a few tables the maxima occur at the same concentration at both temperatures. In nearly every case where there is a maximum there is a slight decrease in conductivity, then a rapid increase as dilution increases, thus giving an inflection in the curve.

Figs. II to IV give the curves for the conductivities of potas-

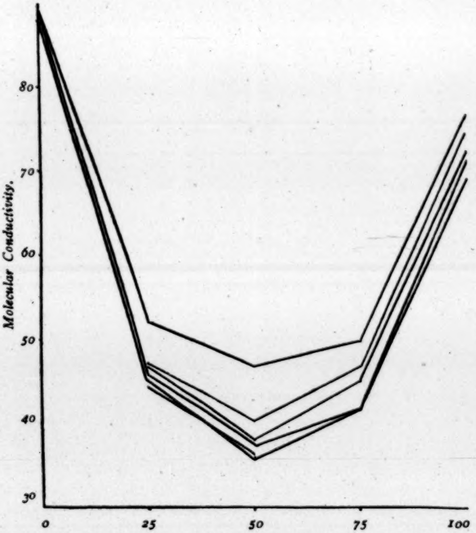

Fig. II.—Conductivity of potassium iodide in mixtures of methyl alcohol and water at 0°.

sium iodide in mixtures of methyl alcohol and water and of ethyl alcohol and water. The abscissas represent the percentage of alcohol and the ordinates represent the conductivity.

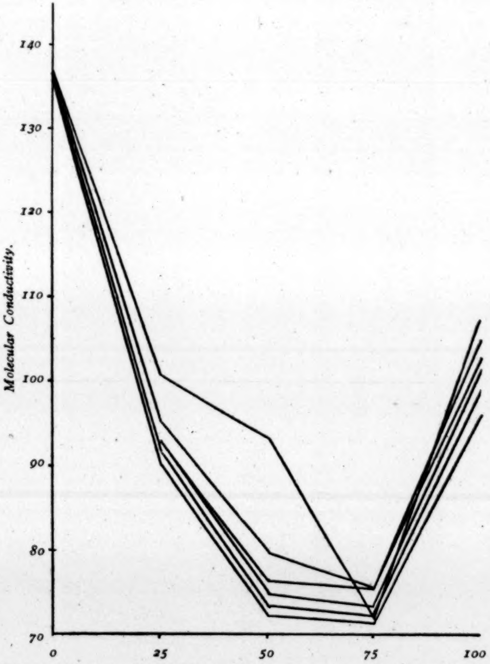

Fig. III.—Conductivity of potassium iodide in mixtures of methyl alcohol and water at 25°.

In Fig. II there is a marked minimum with 50 per cent. methyl alcohol. Fig. III shows a minimum with 75 per cent. methyl alcohol. Fig. IV for potassium iodide in methyl alcohol-water mixtures shows the same characteristics. Fig.

V shows a minimum for only three concentrations; these are with 75 per cent. ethyl alcohol.

Figs. VI to IX are the curves for the conductivity of cobalt chloride in methyl alcohol-water mixtures and ethyl alcohol-water mixtures at both 0° and 25°. Fig. VI shows a minimum with 50 per cent. methyl alcohol. Fig. VII shows minima in the curves with 75 per cent. methyl alcohol. In Figs. VIII and IX there is no minimum.

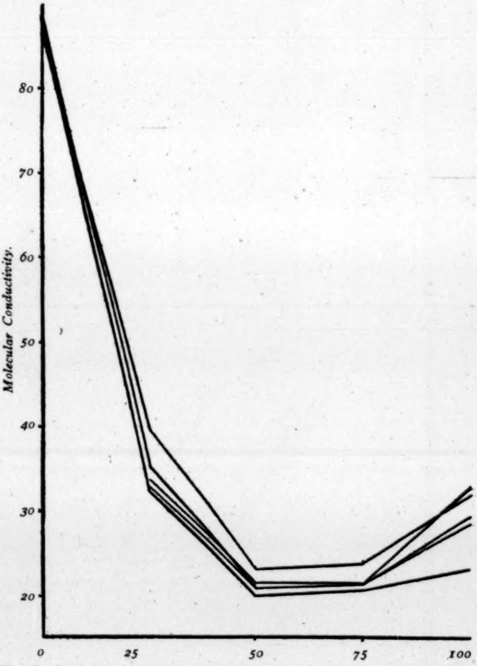

Fig. IV.—Conductivity of potassium iodide in mixtures of ethyl alcohol and water at 0°.

Tables XXIX to XXXVI represent the values for the conductivities of potassium iodide and cobalt chloride in mixed solvents, arranged according to temperature. The proportions in which the solvents are mixed and the concentrations vary. A study of the maxima of conductivity in these tables is interesting. The more probable values for μ_∞ are indicated by a (*). By means of these values we have calculated the dis-

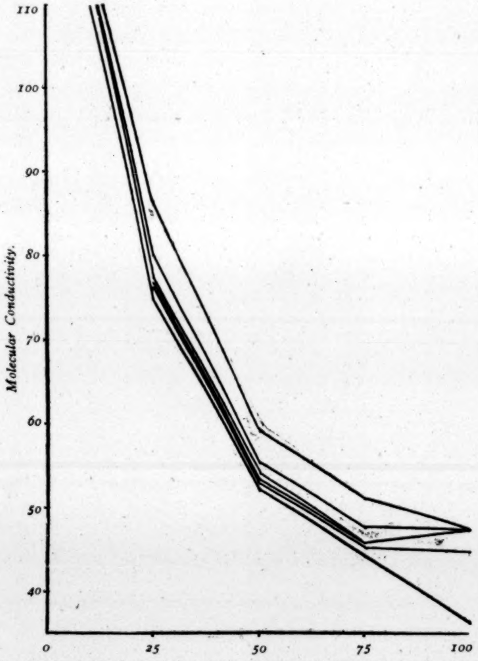

Fig. V.—Conductivity of potassium iodide in mixtures of ethyl alcohol and water at 25°.

sociation of the salts at different volumes for four of these tables (XXIX, XXXI, XXXIII, and XXXV), since these present more μ_∞ values than the rest. We have used the well-known equation, $\alpha = \frac{\mu_v}{\mu_\infty}$ and the values for α are given in Tables XXXVII to XL. In Table XXXIII no μ_∞ occurs for 50 per cent. methyl alcohol-water mixtures.

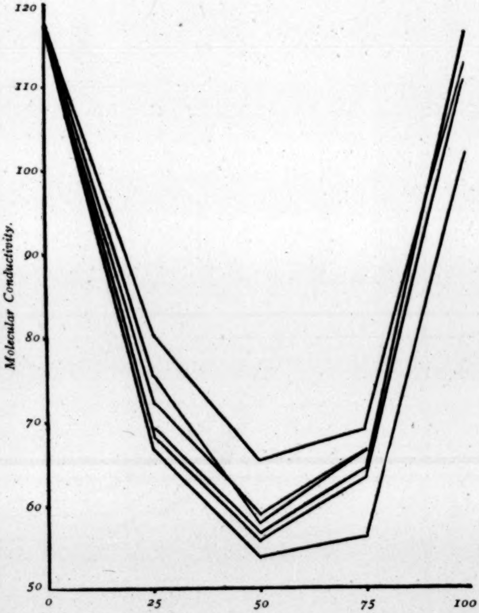

Fig. VI.—Conductivity of cobalt chloride in mixtures of methyl alcohol and water at 0°.

These values for dissociation are interesting when compared with the values for the corresponding molecular conductivities. Fig. X gives the curves for dissociation corresponding to the molecular conductivity as indicated by the curves in Fig. IV. Fig. XI in the same manner corresponds to Fig. VI and Fig. XII to Fig. VIII.

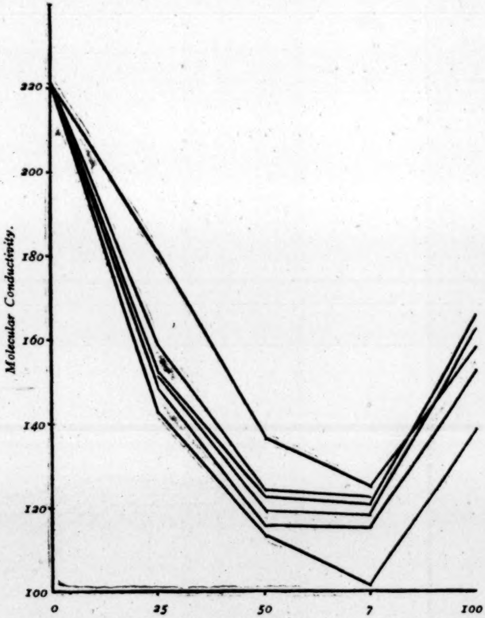

Fig. VII.—Conductivity of cobalt chloride in mixtures of methyl alcohol and water at 25°.

In Fig. IV the conductivity curves of potassium iodide in ethyl alcohol-water mixtures at 0° show minima for all dilutions, while the corresponding curves for dissociation in Fig. X at first rise. If the equation $\alpha = \frac{\mu_v}{\mu}$ holds for mixed solvents this would indicate that at 0° the dissociation in 25 per cent. ethyl alcohol-water mixtures is slightly greater than in pure water. In all mixtures the dissociation is very much greater than it is in pure alcohol.

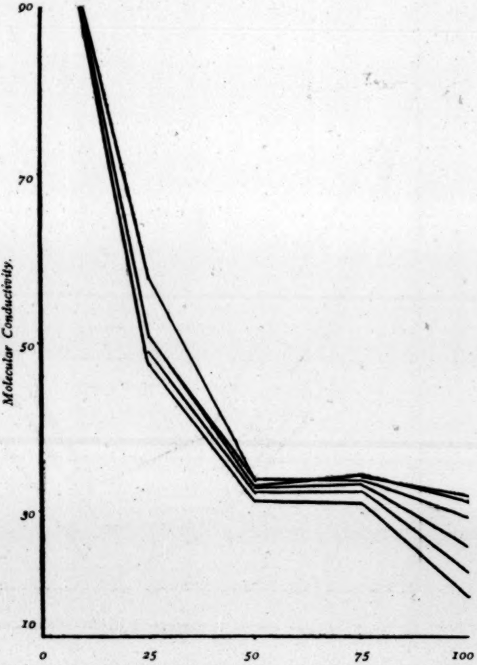

Fig. VIII.—Conductivity of cobalt chloride in mixtures of ethyl alcohol and water at 0°.

Fig. XI gives the curves for cobalt chloride in methyl alcohol-water mixtures corresponding to the molecular conductivity as represented by Fig. VI. The curves for dissociation show minima, but the drop below the straight line of averages is very small when compared with the large and decided minima in Fig. VI.

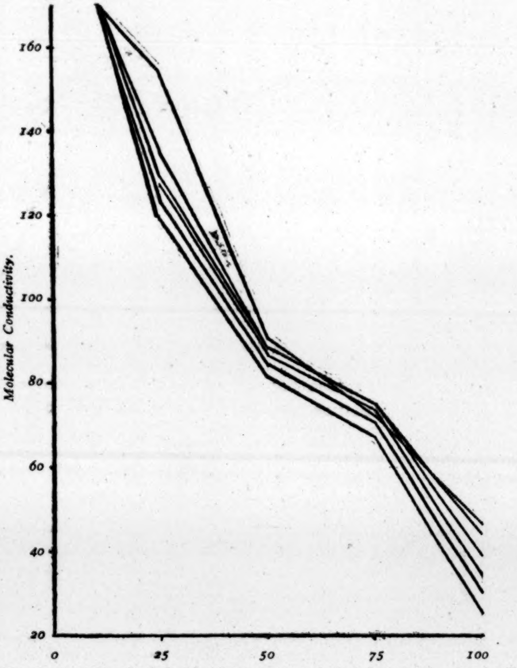

Fig. IX.—Conductivity of cobalt chloride in mixtures of ethyl alcohol and water at 25°.

Fig. XII for dissociation corresponds to Fig. VIII for molecular conductivity. The relation between these two figures is similar to the relation between X and IX. In both cases the mixed solvents are ethyl alcohol and water. In this case we have a binary salt, and the curves for Figs. X and XII are strikingly similar.

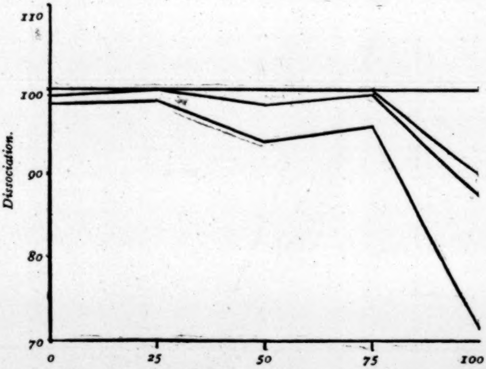

Fig. X.—Dissociation of potassium iodide in mixtures of ethyl alcohol and water at 0°.

The curves representing dissociation in ethyl alcohol-water mixtures are sometimes upward curves, taking a direction opposite to that of the curves representing conductivity, which are downward curves. This fact is especially apparent when Fig. IV,

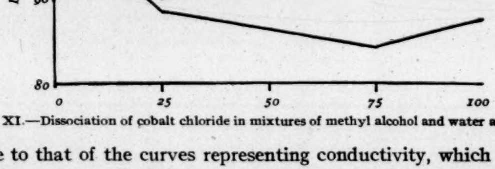

Fig. XI.—Dissociation of cobalt chloride in mixtures of methyl alcohol and water at 0°.

giving the curves for the conductivity of potassium iodide in mixtures of ethyl alcohol and water at 0°, is compared with Fig. X, which gives the curves for the dissociation of these same solutions. This plainly indicates that the greatly diminished conductivity in mixed solvents is due not to diminished dissociation but to the other factor conditioning conductivity, *viz.*, diminished velocity of the ions through the solution. Though it had been previously pointed out that this diminished conductivity is due almost entirely to increased viscosity of the mixed solvent, it was not definitely known what the magnitude of the dissociation in these mixed solvents is, nor was it suspected that this dissociation might be greater in the mixed than in the pure solvents, as is shown to be the case by the curves for dissociation, some of these curves having maxima while those of conductivity have decided minima. These facts are quite marked where ethyl alcohol-water mixtures are used

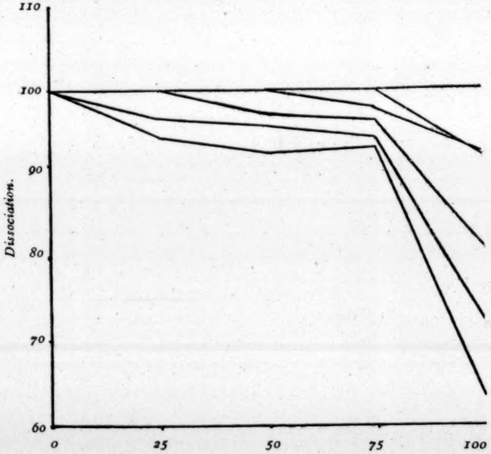

Fig. XII.—Dissociation of cobalt chloride in mixtures of ethyl alcohol and water at 0°.

as solvents. In such cases the increased viscosity, on the one hand, diminishes the conductivity, and the decreased dissociation, on the other, increases the conductivity. The viscosity in this case, since it is the more potent factor, causes the large minima in the curves for conductivity. These minima would be more marked than they are were it not for the slightly increased dissociation.

Table XLI gives the μ_∞ values of molecular conductivity for the various salts studied both in methyl and in ethyl alcohols at 0° and at 25°, whenever such values could be found. The values without the brackets were determined experimentally. Those within the brackets could not be determined experimentally because of the great dilutions and consequently unavoidable errors, but were calculated by a method given below.

An examination of the table reveals the fact that there is some relation between the maximum for each salt in the different solvents at any given temperature. It was suspected that this relation is a constant and that the following equation would hold:

$$\frac{\mu_\infty \text{ methyl}}{\mu_\infty \text{ ethyl}} = \text{constant.}$$

This equation was then applied with the following results:

Binary Electrolytes.

$LiNO_3$ at	0°	= 2.37.
NaI	0°	= 2.37.
NH_4Br	25°	= 2.44.
NaI	25°	= 2.17.

Ternary Electrolytes.

$CoCl_2$ at 0° = 3.68.

These facts make it appear probable that there is approximately such a constant for binary electrolytes and another for ternary electrolytes. These data are not sufficient, however, to give a final value to such constants. Further investigations will be required for this purpose. Most of these maxima occur at dilutions of $V = 12{,}800$ to $V = 51{,}200$. At these dilutions it is very difficult to obtain accurate results and the values for the constant are probably within the limits of experimental error.

The value for the constant between methyl and ethyl alcohols for binary electrolytes appears to be very nearly 2.37. We have obtained but one value for ternary electrolytes, which is 3.68. That is nearly 1.5 × 2.37. The latter value (3.56) is probably the more nearly correct. The factor 1.5 is employed since this expresses the ratio of ions present between binary and ternary electrolytes at complete dissociation.

With the data in hand we proceed to test further the accuracy of the above equation by supplying by calculation in Table XLI those μ_∞ values which could not be determined experimentally. The value of the constant was taken as 2.37 for binary electrolytes and 3.56 for ternary electrolytes. The calculated value for potassium iodide in methyl alcohol at 0° from the value in ethyl alcohol would be 77.5. An examination of Table I reveals the fact that this value is probably very nearly correct. For 25° it would be 112.6. Again from the same table this is probably correct. Ammonium bromide in ethyl alcohol at 0° would be equal to 30.3. This too as indicated by Table IV is probably nearly correct. Potassium sulphocyanate in methyl alcohol at 25° would have a value of 110.4. Table V indicates that this value is probably correct within the limits of experimental error. Lithium nitrate gives a value of 96.7 in methyl alcohol at 25°; compared with Table VII this would seem to be nearly correct.

With ternary electrolytes there are only three cases to which this equation can be applied. Copper chloride in ethyl alcohol at 0° would give a value of 24.8, and cobalt chloride in ethyl alcohol at 25° would give 46.7 as the value for the maximum in conductivity. In Table XIV, at 0°, a maximum is reached at $V = 25600$. The maxima at the different temperatures as a rule do not occur very far apart. We believe that the value 46.7 is pretty nearly correct for the maximum for cobalt chloride in ethyl alcohol at 25°. The only two values which do not fit into the table are the value for potassium cyanide in methyl alcohol at 0° and that for copper chloride in ethyl alcohol at 25°. The latter, however, is not far from what we might expect it to be.

We believe from the above results that the ratio between the maxima in molecular conductivity for different salts in methyl alcohol and the maxima for the same salts in ethyl alcohol is probably constant for all binary electrolytes, that for all ternary electrolytes it is a constant of different value, and that there is a definite relation between these two constants.

Jones, in an article on "The Electrolytic Dissociation of Certain Salts in Methyl and Ethyl Alcohols, as Measured by the Boiling-Point Method," gives the following table which expresses "the dissociation values of the above alcohols as calculated from data obtained by the boiling-point method." The ratios of these values were calculated and are also expressed in the table:

Table XLVII.

Substance.	Dilution normal.	Dissociation in methyl alcohol. Per cent.	Dissociation in ethyl alcohol. Per cent.	Ratio.
KI	0.1	52	25	2.08
NaI	0.1	60	33	1.8
NaBr	0.1	60	24	2.5
NH_4Br	0.2	49	21	2.3
CH_3COOK	0.1	36	16	2.3
CH_3COONa	0.1	38	14	2.7
$Ca(NO_3)_2$	0.1	15	5	3.0

Leaving out the value 1.8 for sodium iodide, which is evidently erroneous, we obtain as a mean from the other values of the binary electrolytes 2.37 which, it will be remembered, is the same as the value obtained above by the conductivity method for the ratio between the maxima in the different alcohols. The value in this table for the one ternary electrolyte is not so great as that determined by the conductivity method, and yet it is possible that more data would give comparable values.

The boiling-point data in this work were obtained by means of the boiling-point apparatus used by Jones.[1] Both solvents were carefully purified and dried.

Table XLIV gives the dissociation of certain salts as calculated by both the conductivity and boiling-point methods:

Table XLIV.

Salt.	Solvent.	Dissociation from conductivity method. Per cent.	Dissociation from boiling-point method. Per cent.
KI	Methyl	65	49
KI	Ethyl	49	26
NaI	Methyl	75	61
NH_4Br	Methyl	71	47
NH_4Br	Ethyl	40	20

It will be seen at a glance from the above table that the dissociation values as determined by conductivity are higher than those found by the boiling-point method, in both methyl and ethyl alcohols. This may possibly be due to a polymerization of the undissociated molecules in the solvent in question. This would give too low dissociation as measured by the boiling-point method, since this method takes into account both the molecules and the ions, while the conductivity method deals only with the ions.

SUMMARY.

We have measured the conductivity of various salts in pure methyl and ethyl alcohols at very high dilutions, and also in mixtures of methyl and ethyl alcohols with water. In many of these measurements we have found the value of μ_∞.

Many of these values were found to occur at concentrations between $V = 3200$ and $V = 51200$.

A constant ratio was found between the values of μ_∞ for several binary electrolytes in methyl alcohol and in ethyl alcohol, and the ratio for one ternary electrolyte was worked out. These facts indicate that there is a definite relation between these two ratios.

We have found minima in most of the curves for mixed solvents.

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[1] Z. physik. Chem., **31**, 114 (1899) (Jubelband zu van't Hoff).

We have tabulated the dissociation of several salts in methyl alcohol and ethyl alcohol as determined by the boiling-point method.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
June 1910.

REVIEWS.

THE VEGETABLE PROTEINS. By THOMAS B. OSBORNE, PH.D., Research Chemist in the Connecticut Agricultural Experiment Station, New Haven, Connecticut. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1909. pp. xiii + 125.

This work forms one of the series of excellent monographs on biochemical subjects appearing under the editorship of Messrs. Hopkins and Plimmer. The editors are to be congratulated upon securing the services of Dr. Osborne for writing the section devoted to the vegetable proteins. Dr. Osborne has contributed so largely to the investigation of the vegetable proteins by precise chemical methods that most of the questions discussed in the present volume are based upon his own investigations. The writer has wisely thought it more important to discuss the general physical and chemical properties of the vegetable proteins rather than to give a detailed descriptive account of the individual substances.

A chapter in which the subjects of toxalbumins, anaphalaxis and related topics are lightly touched upon in so far as they relate to the vegetable proteins forms the concluding section of a truly admirable monograph. W. D. DAKIN.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS, Volumes II and III. Fourth edition. Philadelphia: P. Blakiston's Son & Co. 1910. pp. x + 520 and x + 635. Price, $5.00 per volume.

These two volumes cover the ground of Parts I and II and a portion of Part III of volume II of the third edition and show an increase of about 300 pages in the text devoted to the subjects covered.

Volume II is edited by Henry Leffmann and W. A. Davis, Volume III by W. A. Davis and Samuel S. Sadtler. In both cases a number of authors have contributed to the revision of the text, the sections and authors being as follows: Volume II, Fixed oils, fats and waxes (Mitchell); Special characters and Methods (Archbutt); Butter fat (Revis and Bolton); Lard (Mitchell); Linseed oil (Klein); Higher fatty acids (Robertson); Soap (Leffmann); Glycerol (Davis); Cholesterols (Gardner); Wool fat, cloth oils (Gill). Volume III, Hydrocarbons (Garrett); Bitumens (Sadtler); Naphthalene and its derivatives (Davis); Anthracene and its associates (Sadtler); Phenols (Sadtler); Aromatic acids (Horton); Gallic acid and its allies (Dreaper); Phthalic acids and the phthaleins (Davis); Modern explosives (Marshall).

As in earlier editions, many sections consist as largely of descriptive material as of analytical methods. In some of the sections the treatment follows that of the third edition so closely as to suggest that the revision was here accomplished by piece-meal insertions rather than by a thorough rewriting. As a rule, however, close examination shows numerous inconspicuous changes in older portions of the text and makes it appear that the revisers have done their work conscientiously but sometimes too conservatively. In some cases material which is now rather antiquated is retained in full while the newer work on the same topic is given very incompletely. On the other hand, no part of the work is wholly lacking in modern material and recent references and certain sections have been thoroughly revised and brought well up to date.

The descriptions of individual oils, fats and waxes, which occupy a large part of Volume II, are of great value. This part of the text has been more than doubled in extent and now covers about 300 pages.

In view of the paucity of convenient literature on American petroleum it is fortunate that the section on Bitumens (which includes petroleum and its products) has been expanded at least one-third, largely by the introduction of American material.

In the section on Phenols considerable attention is appropriately given to the subject of the examination of creosote oils for timber preservation.

In printing and binding this edition is a decided improvement over the last and there are not many typographical errors, but some obviously incorrect data were noted in Volume II (*viz.*, for the saponification number and saponification equivalent of linolein on page 17, and the flashing point of linseed oil attributed to Rakusin on page 331) and the headings and placing of new material are not always in harmony with the classification of the old. Partly for this reason and partly because the work is likely to be used more for reference than for consecutive reading a more detailed index might be advantageous.

The work as a whole is to be heartily welcomed. Since certain large fields of organic analysis are now so well covered by special reference books, this new edition of Allen cannot be expected to occupy the unique position which was held in its day by the original treatise, but it is one of the works which should be at the hand of every chemist who has to do with the analysis of either natural or manufactured organic materials. H. C. S.

THE YEAR-BOOK FOR COLORISTS AND DYERS, Presenting a Review of the Year's Advances in the Bleaching, Dyeing, Printing and Finishing of Textiles. By HERMANN A. METZ. Volume XII. New York: Hermann A. Metz, 122 Hudson Street. 1909. pp. 388.

The volume contains reference tables, patents for the year 1909, notes on processes, new colors, etc., a long list of dyestuffs with the name of the maker, and reference to dyeing methods in addition to miscellaneous matter. The volume is, without doubt, useful to dyers and textile chemists. The list of schools giving courses in textile chemistry or dyeing is by no means complete. One has no right, however, to expect this in works of this kind. G. S. F.

IDENTIFICATION OF THE COMMERCIAL DYE-STUFFS, Being Vol. III of a Method for the Identification of Pure Organic Compounds by a Systematic Analytical Procedure Based on Physical Properties and Chemical Reactions. Containing Classified Original Descriptions of Nearly 1700 Synthetic and Natural Dye-Stuffs; References to Many Allied Brands; Suggestions on the Examination of Dye-Stuffs in Mixtures; and a Color Standard. BY SAMUEL PARSONS MULLIKEN, PH.D., Assistant Professor of Organic Chemical Research at the Massachusetts Institute of Technology, Boston, Mass. New York: John Wiley & Sons; London: Chapman and Hall, Limited. 1910. pp. vi + 274. Price, $5.00.

This book contains original descriptions of nearly 1700 dye stuffs, and is intended to provide for their identification, chiefly in the powder or paste form. The dye stuffs are first tested for homogeneity, divided into groups according to their behavior towards textiles, and to their other properties, and then identified by means of further tests. The entire process appears to be long and tedious, but the exact identification of one out of seventeen hundred dye stuffs cannot well be a rapid process. No doubt dye stuff chemists have shorter tests and methods, which are, however, based upon their knowledge and experience as to colors and appearances and are difficult to reduce to writing. Dr. Mulliken's book has the appearance of a very tedious piece of work, well done, and will no doubt be useful to those who need to identify dyestuffs.

G. S. F.